



Work done
in reversible
processes

Some
material
properties

Work done in reversible processes

In general can write

$$dW = Xdx$$

Generalised force

Conjugate displacement

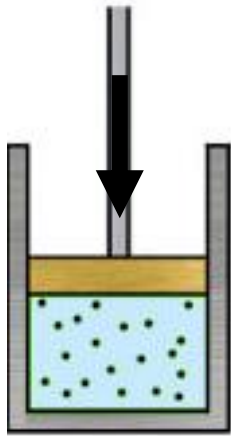
$$\Delta W = \int_i^f Xdx$$

Work done in reversible processes

System	X (intensive variable)	x (extensive variable)	Work done
Hydrostatic pressure	Pressure p	Volume V	$-pdV$
Surface film	Surface tension γ	Area of film A	γdA
Stretching a wire	Tension τ	Wire length l	τdl
Magnetised material	Magnetic field \mathbf{B}	Magnetic moment \mathbf{m}	$\mathbf{B}d\mathbf{m}$
Electric current	Potential difference \mathcal{E}	Charge Z	$\mathcal{E} dZ$
Generalised force	Generalised force X	Conjugate displacement x	Xdx

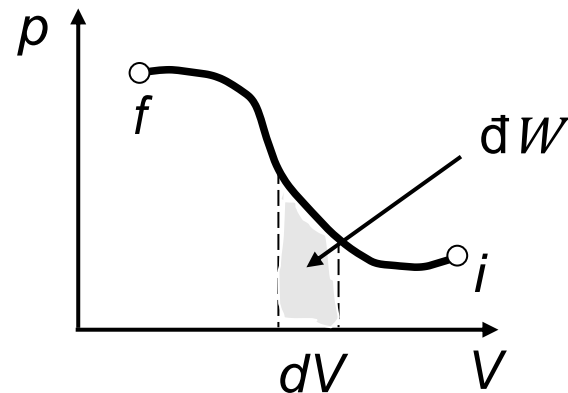
Gas in a box

$$F = pA$$



$$\delta W = -Fdx = -pAdx = -pdV$$

$$\Delta W = -\int_i^f pdV$$



So first law for reversible change with hydrostatic pressure can be written as $dU = \delta Q + \delta W = \delta Q - pdV$

Some material properties

For hydrostatic pressure $V = V(p, T)$

$$dV = \left(\frac{\partial V}{\partial p} \right)_T dp + \left(\frac{\partial V}{\partial T} \right)_p dT$$
$$= -V\kappa_T dp + V\beta_p dT$$

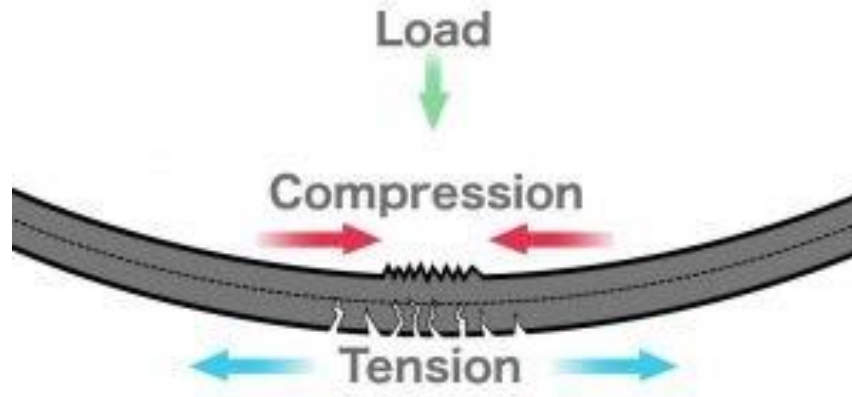
κ_T = isothermal compressibility $\equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \equiv \frac{1}{B_T}$

B_T = Bulk modulus

β_p = thermal expansion coefficient $\equiv +\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$

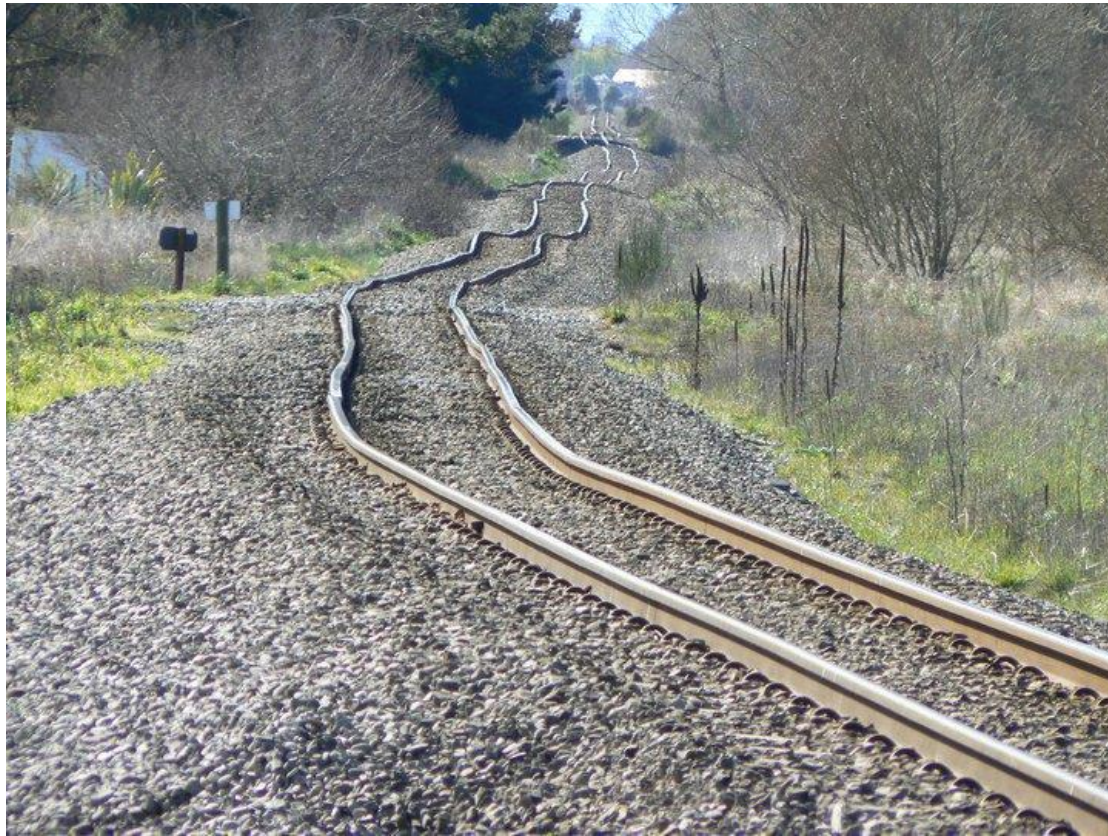
$$\Delta W = - \int p dV = \int_{p_1}^{p_2} p \kappa_T V dp - \int_{T_1}^{T_2} p \beta_p V dT$$

Isothermal compressibility, κ_T



Picture taken from Wikipedia

Coefficient of thermal expansion, β_p



Example: Q8 & 9 problem sheet

Write down a suitable definition for a linear coefficient of thermal expansion α of an object. If α is independent of temperature and pressure, then show that the length l of the object is given by

$$l = l_0 \exp(\alpha \Delta T).$$

Is it possible for α for a material to be zero? Is it possible for α to be negative?

$$\alpha = \text{var} \frac{dl}{dT}$$

$\text{var} = 1/l$ is necessary to make the coefficient independent of the initial length, i.e. we want to calculate the fractional change

$$\alpha = \frac{1}{l} \frac{dl}{dT}$$

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$$\alpha = \frac{1}{l} \frac{dl}{dT}$$

$$\alpha dT = \frac{1}{l} dl$$

$$\int_{T_0}^T \alpha dT = \int_{l_0}^l \frac{1}{l} dl$$

$$\alpha(T - T_0) = \ln \frac{l}{l_0}$$

$$l = l_0 \exp(\alpha \Delta T)$$

Coefficient of thermal expansion, β_p



Isothermal compression of a solid

$$\Delta W = - \int p dV = \int_{p_1}^{p_2} p \kappa_T V dp - \int_{T_1}^{T_2} p \beta_p V dT$$
$$\Delta W = \int_{p_1}^{p_2} p \kappa_T V dp \cong \frac{1}{2} \kappa_T \bar{V} (p_2^2 - p_1^2)$$

Volume and κ_T nearly constant for a solid

Isobaric change in a solid

$$\Delta W = - \int p dV = \int_{p_1}^{p_2} p \kappa_T V dp - \int_{T_1}^{T_2} p \beta_p V dT$$
$$\Delta W = - \int_{T_1}^{T_2} p \beta_p V dT = -p \bar{V} \beta_p (T_2 - T_1)$$

Volume and β_p nearly constant for a solid

Isothermal compression of an ideal gas

$$\Delta W = - \int p dV$$

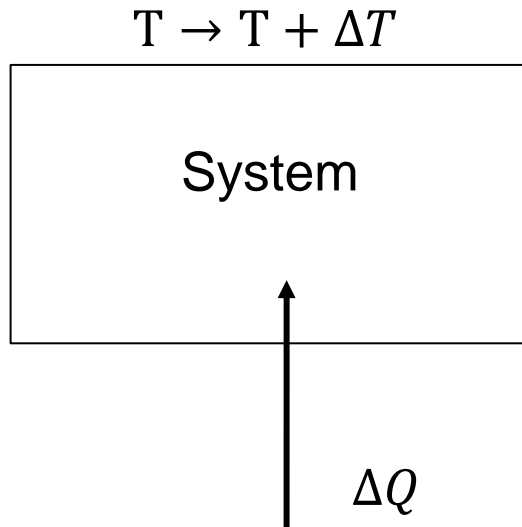
$$\Delta W = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{p_2}{p_1}$$

$$\Delta W = -nRT \ln \frac{V_2}{V_1}$$

$$pV = nRT \Rightarrow V = \frac{nRT}{p}$$

$$\Delta W = -nRT \ln \frac{p_1}{p_2} = nRT \ln \frac{p_2}{p_1}$$

Heat capacity



Reversible process

$$C = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta Q}{\Delta T} \right) = \frac{dQ}{dT} \text{ (extensive)}$$

Depends on conditions

Heat capacity at constant volume $C_V = \left(\frac{dQ}{dT} \right)_V$

Heat capacity at constant pressure $C_p = \left(\frac{dQ}{dT} \right)_p$

i.e. $C = C(V, p)$

Specific heat capacity: $c_p = \frac{1}{m} \left(\frac{dQ}{dT} \right)_p$ and $c_V = \frac{1}{m} \left(\frac{dQ}{dT} \right)_V$

Heat capacity - Enthalpy

$$\delta Q = dU - \delta W = dU + p dV$$

$$\text{Hence } C_V = \left(\frac{\delta Q}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \text{ and } C_p = \left(\frac{\delta Q}{dT} \right)_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p$$

At constant pressure $p dV = d(pV)$

$$\therefore \delta Q = dU + p dV = dU + d(pV) = d(U + pV)$$

$H \equiv U + pV = \text{Enthalpy}$ (or heat function at constant pressure)

H is function of state, dH is exact

$$dH = dU + p dV + V dp = \delta Q + V dp$$

$$C_p = \left(\frac{\delta Q}{dT} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p$$

Heat capacity, who cares?

Weather:

Earth's surface $\sim 3/4$ water rest rock

$c_{\text{water}} \sim 4\text{-}5 \times c_{\text{rock}}$

water heats up slower than rock, but then retains heat for longer

Swimmer vs runner:

heat capacity of water 4.5 times that of air

athlete has body temperature of 37°C

Swimmer will burn more calories, to retain body temperature

Cooling:

Air conditioners contain water as coolant, because it takes more energy to heat a certain volume of water compared to air