2.5 Work

Applying the general definition of differential work to an expansion against a constant external pressure p_{ex} we find for the expansion work

$$dw = -\vec{F}d\vec{z} = -p_{ex}Adz = -p_{ex}dV \quad \text{, i.e.} \quad w = -\int_{V_1}^{V_2} p_{ex}dV = -p_{ex}\Delta V \tag{2.13}$$

Note: EXPANSION work has to do with:

1. EXTERNAL pressure.
2. Change in volume of the system.
3. The sign is given by convention, work done by the system is negative.
4. In general w is path dependent.

Examples for expansion work are

- Joule experiment, i.e. free expansion (against $p_{ex} = 0$). $w = 0$, but $dU = \delta q \neq 0$. Obviously any derivative of energy with respect to volume has the dimension of pressure which motivates the meaning of $\partial U/\partial V$ to be an "internal pressure".
- Expansion against constant pressure:

$$w = -\int_{V_1}^{V_2} p_{ex}dV = -p_{ex}\Delta V \tag{2.14}$$

  (rectangular area in a $p - V$ diagram).
- Reversible and isothermal expansion:

$$\delta w = -p_{ex}dV = -pdV \quad \text{(internal pressure = external pressure for reversible changes)} \tag{2.15}$$

  p and V change, thus a thermal equation of state is needed. As an example we use the perfect gas equation

$$w = -\int_{V_1}^{V_2} pdV = -n\,R\,T\int_{V_1}^{V_2} \frac{dV}{V} = -n\,R\,T\ln\frac{V_2}{V_1} \tag{2.16}$$

Several types of parameter pairs exist whose product represents an energy:

Type of work	dw	Comment
Expansion	$-p_{ex}\,dV$	external pressure, volume change
Surface expansion	$\gamma\,d\sigma$	surface tension, area change
Extension	$f\,dl$	tension, length change
Electrostatic	$\Phi\,dq$	electrical potential, charge change
Electrical field	$\vec{E}\,d\vec{P}$	electrical field, polarization
Magnetic field	$\vec{H}\,d\vec{M}$	magnetic field, magnetization