Statistical Molecular Thermodynamics

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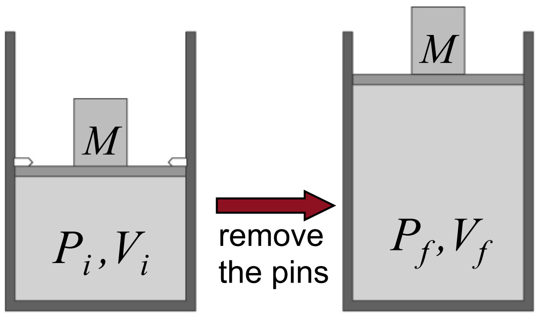
Video 5.2

Paths for *PV* Work

Variations in Pressure



i = initial *f* = final

In this experiment P_{ext} remains constant during the expansion and $w = -P_{\text{ext}}\Delta V$

If P_{ext} is *not* constant during the expansion, the work must be computed as the integral over the path from P_i, V_i to P_f, V_f, *and one must know how P_{ext} varies with V*,

$$w = -\int_{V_i}^{V_f} P_{\text{ext}} dV$$

A fully general expression

For constant P_{ext}, we recover $w = -P_{\text{ext}}\int_{V_i}^{V_f} dV = -P_{\text{ext}}\left(V_f - V_i\right) = -P_{\text{ext}}\Delta V$

Work Is Area Under a $P_{ext}V$ Curve

Noting the relationship between a one-dimensional integral and geometric area, work (w) is the area under the P_{ext} vs. V curve,

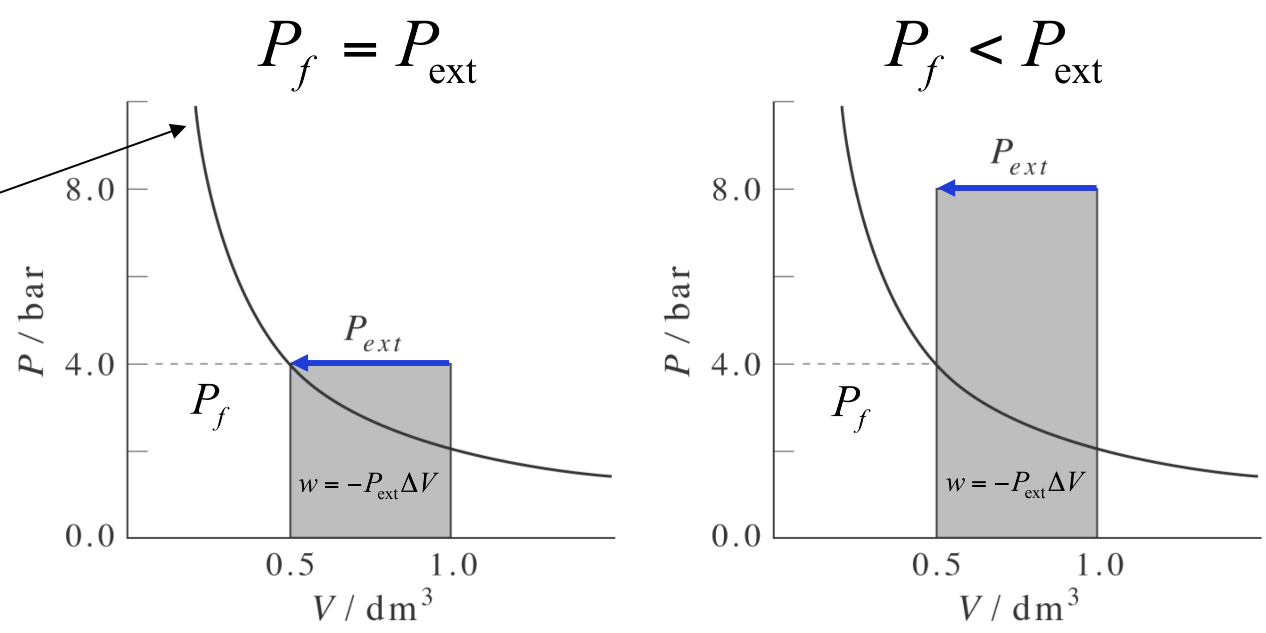
$$w = -\int_{V_i}^{V_f} P_{ext}\, dV$$

Consider an *isothermal compression at constant pressure* P_{ext}

Curve for an ideal gas, at constant T

$$P = \frac{nRT}{V} \propto \frac{1}{V}$$

The work is equal to the shaded areas and depends on P_{ext}.

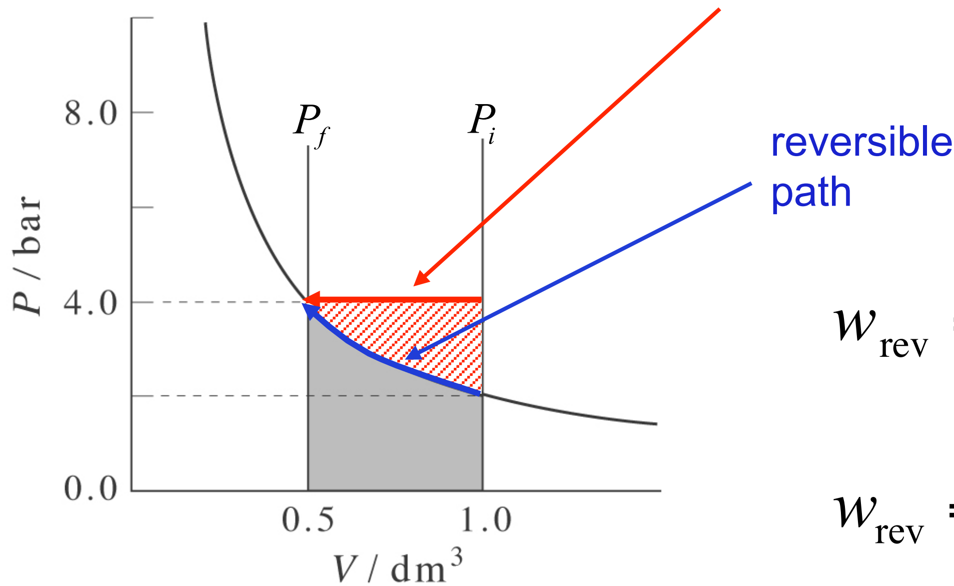


(a) (b)

Reversible Isothermal Compression

Work *depends on the path* taken from V_1 to V_2. For a compression, *the minimum work is done along the reversible path*. In infinitesimally small steps, P_{ext} is made infinitesimally larger than P_{gas}. Thus, at every step P_{ext} is *equal* to the *equilibrium* gas pressure P_{gas},

$P_{ext} = P_f \Rightarrow$ Constant P_{ext} path with minimum w



$$w_{rev} = -\int_{V_1}^{V_2} P_{gas}\,dV$$

$$\left(\text{ideal gas}: P_{gas} = \frac{nRT}{V}\right)$$

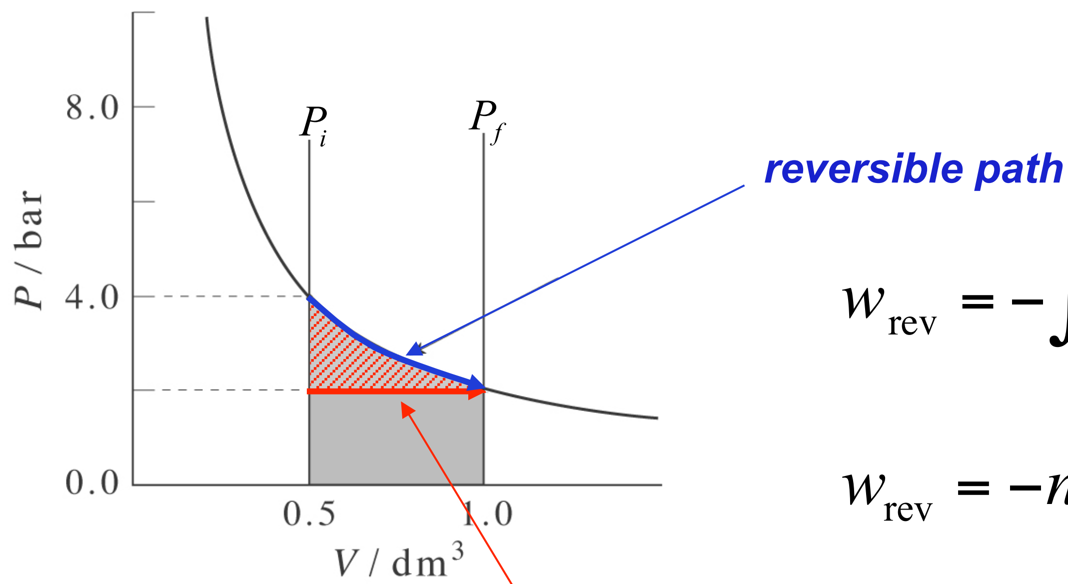
$$w_{rev} = -\int_{V_1}^{V_2} \frac{nRT}{V}\,dV = -nRT\int_{V_1}^{V_2} \frac{dV}{V}$$

$$w_{rev} = -nRT\ln\frac{V_2}{V_1}$$

Compression implies $V_2 < V_1$ so work is positive, as it should be

Reversible Isothermal Expansion

For an expansion, *the maximum work is done on the surroundings along the reversible path*. It is the same work (with opposite sign) as that required for compression when traveling in the opposite direction. Thus, it is indeed a *reversible* path.



$$w_{rev} = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

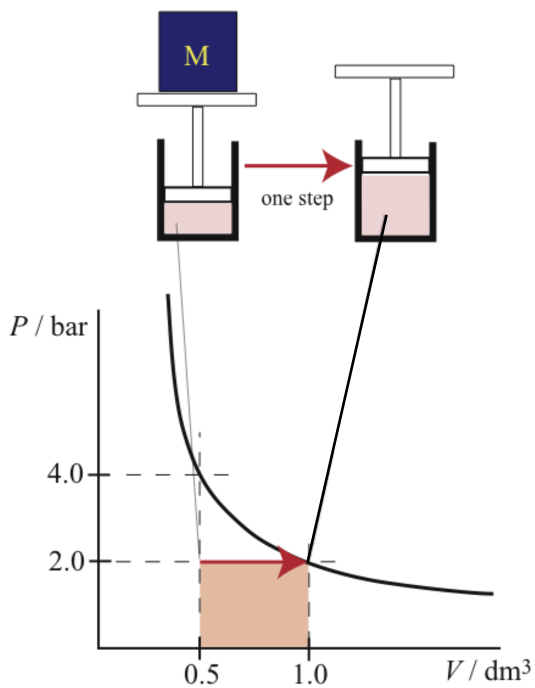
$$w_{rev} = -nRT \ln \frac{V_2}{V_1}$$

$P_{ext} = P_f$ ⇨ Constant P_{ext} path with maximum w

Expansion implies $V_2 > V_1$ so work is negative

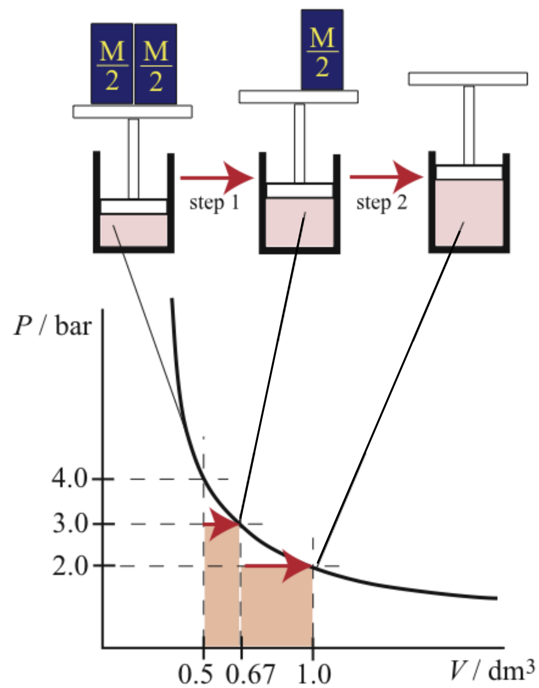
Reversibility As a Limit

Consider three ways to *isothermally* (so $PV = \text{constant}$) expand an ideal gas from $0.5\ \text{dm}^3$ and $4\ \text{bar}$ to $1.0\ \text{dm}^3$ and $2\ \text{bar}$.



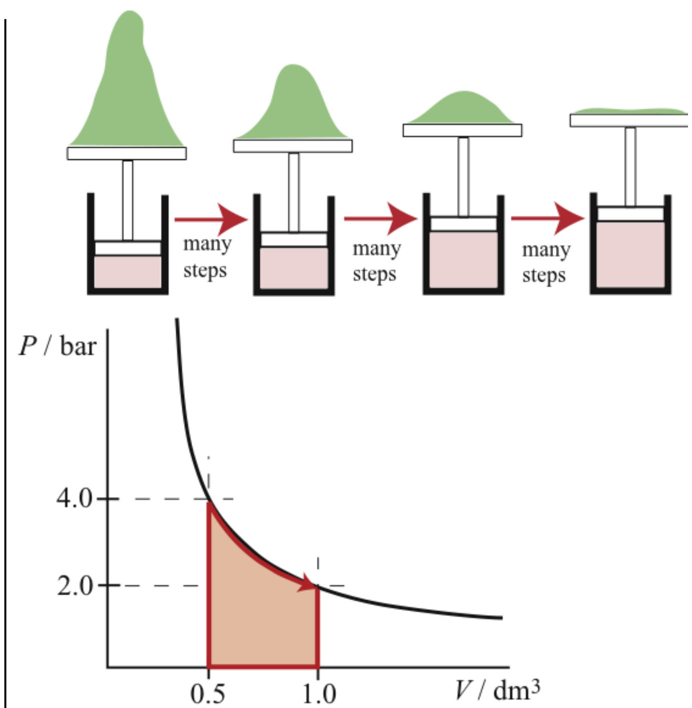
One step

$w = -100\ \text{J}$



Two steps

$w = -117\ \text{J}$



Reversible

$w = -139\ \text{J}$