

Energy, Work and Heat

Energy is the capacity to do work.

Its classification into:

	kinetic	potential
	(by motion)	(by position)
e.g.	thermal	chemical, electrical

Is purely arbitrary!

Heat and **work** are *not* “types” of energy, but are processes involving *transfer* of energy. They appear and disappear at the system boundary. They are **path variables**.

Heat is the transfer of energy from one body to another of lower temperature.

Convention: if heat flows **into** the system, $q > 0$.

Work is the transfer of energy by some mechanism other than temperature difference.

Convention: if work is done **on** the system, $w > 0$.

Heat stimulates random motion.

Work stimulates organized motion.

Work “degrades” into heat.

- qualitative observations by Count Rumford (Ben Thompson)
- quantitative measurements by James Joule

The First Law of Thermodynamics

$q > 0$ for heat flow into the system
 $w > 0$ for work done on the system

- ❖ For finite changes of state: $\Delta U = q + w$
- ❖ For infinitesimal changes: $dU = \delta q + \delta w$

U is the internal energy of the system.

- ❖ When a system changes from one state to another along an adiabatic path, the amount of work done is the same, whatever the means employed.

$$\text{For } q = 0, \quad w_{\text{ad}} = U_{\text{final}} - U_{\text{initial}} = \Delta U$$

$$\text{For } q \neq 0, \quad q = \Delta U - w = w_{\text{ad}} - w$$

- ❖ The energy of an isolated system is constant.

$$\text{For } q = 0, w = 0 \quad \Delta U = 0$$

\Rightarrow *No perpetual motion machines!*

- ❖ In any cyclic transformation the work done by a system on its surroundings is equal to the heat withdrawn from the surroundings.

$$-\oint \delta w = \oint \delta q \quad \Leftrightarrow \quad \oint dU = 0$$

- ❖ The energy of the universe is constant.

$$\Delta U_{\text{system}} = -\Delta U_{\text{surroundings}}$$

Temperature

Two systems in thermal equilibrium are at the same temperature.

If system A is in thermal equilibrium with system B,
and A is in thermal equilibrium with C,
then B must be in thermal equilibrium with C.

This is a statement of the **zeroth law of thermodynamics**.

Ideal gas temperature: $T = \lim_{P \rightarrow 0} \left(\frac{PV}{nR} \right)$

Unit of temperature: $1 \text{ Kelvin} = \frac{T(\text{triple point of water})}{273.16}$

The freezing point of water at 1 atm is 273.15 K.

The boiling point of water at 1 atm is 373.12 K.

The Celsius scale is defined as $t / ^\circ\text{C} = T / \text{K} - 273.15$

It is possible to define an **absolute temperature scale** (**Kelvin scale**) by considering the work done in an isothermal reversible expansion/compression.

$$w = nRT \ln \frac{V_1}{V_2}$$

Pressure–Volume Work 1

Expansion

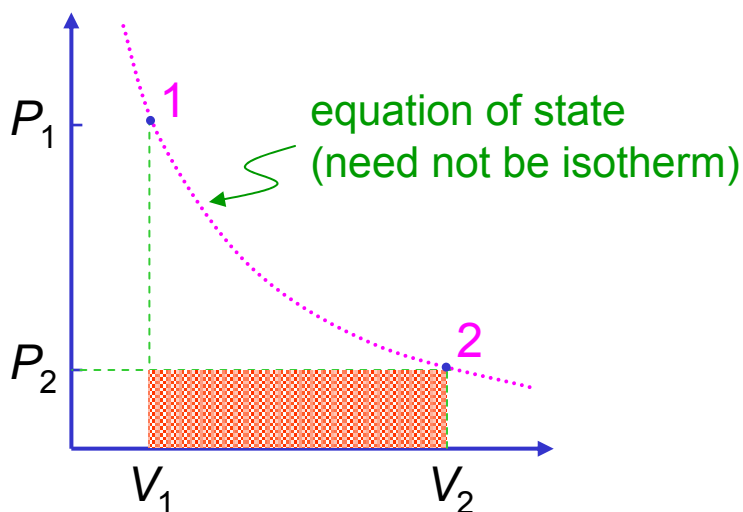
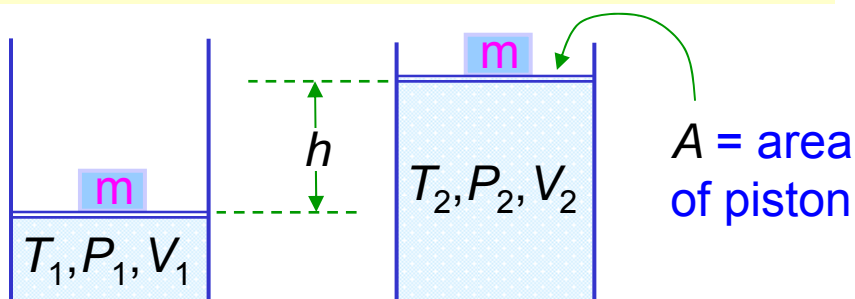
$$P_1 > mg / A$$

$$P_2 = P_{\text{ex}} = mg / A$$

$$w = -(mg)h$$

$$= -(P_{\text{ex}} A)h$$

$$= -P_{\text{ex}} (V_2 - V_1)$$



Expansion into a vacuum

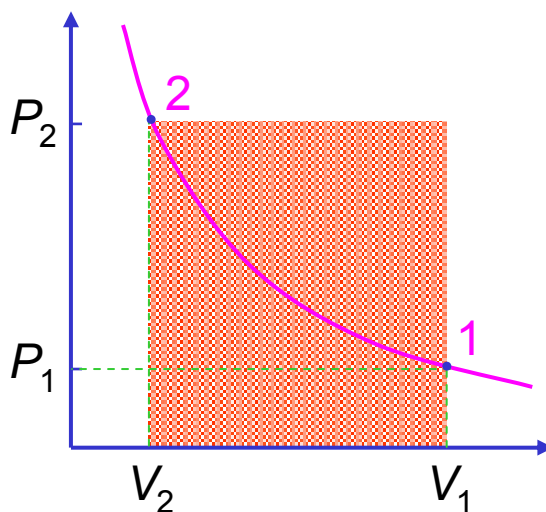
$$P_{\text{ex}} = 0 \Rightarrow w = 0$$

Compression

$$P_1 < P_{\text{ex}}$$

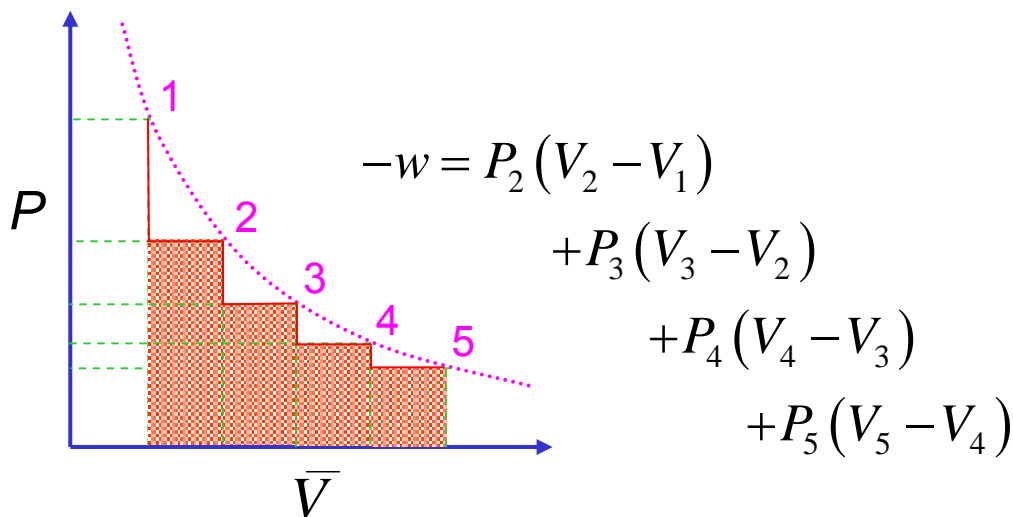
$$P_2 = P_{\text{ex}}$$

$$w = -P_{\text{ex}} (V_2 - V_1)$$



Pressure–Volume Work 2

Multi-stage Expansion



Reversible Expansion

Make steps so small that

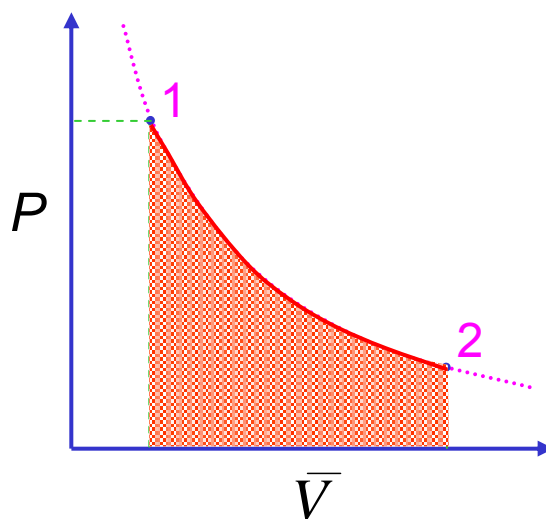
$$dP \rightarrow 0, dV \rightarrow 0$$

Then $-\delta w = P_{\text{ex}} dV$

$$= (P_{\text{int}} + dP) dV$$

$$\rightarrow P_{\text{int}} dV$$

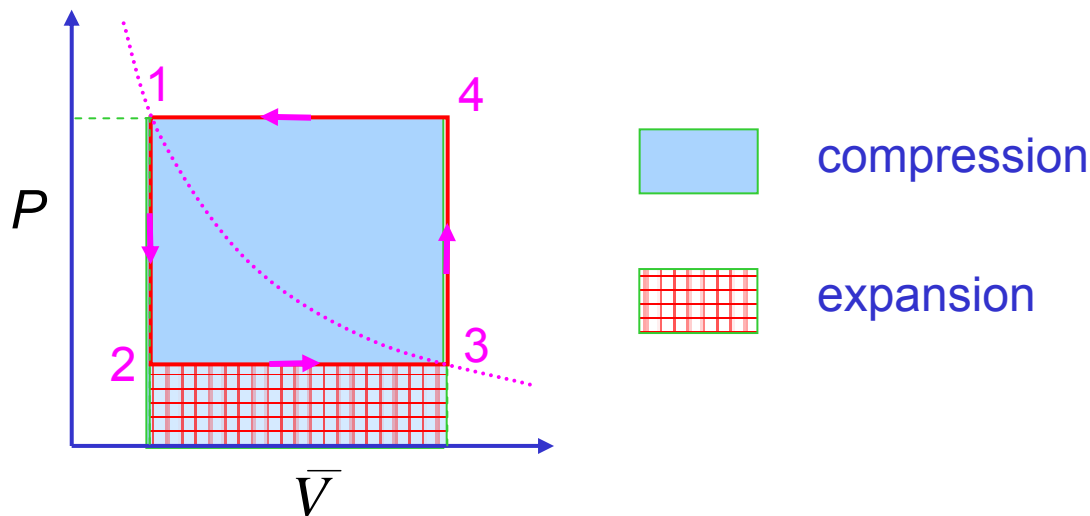
$$w = \int_{\text{path}} dw = - \int_1^2 P_{\text{int}} dV$$



For ideal gases $P_{\text{int}} = nRT/V$

and at fixed temperature $w_{\text{rev}} = -nRT \ln \left(\frac{V_2}{V_1} \right) = nRT \ln \left(\frac{P_2}{P_1} \right)$

Pressure–Volume Work 3



Consider the cyclic path $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$

$$\begin{aligned}
 -w &= 0 + P_3(V_3 - V_1) + 0 + P_1(V_1 - V_3) \\
 &= (P_3 - P_1)(V_3 - V_1)
 \end{aligned}$$

Consider the cyclic reversible path $1 \rightarrow 3 \rightarrow 1$

$$\begin{aligned}
 -w &= \int_{V_1}^{V_3} P dV + \int_{V_3}^{V_1} P dV \\
 &= \int_{V_1}^{V_3} P dV - \int_{V_1}^{V_3} P dV = 0
 \end{aligned}$$

Even for a cyclic process w depends on path

$$\oint dU = 0 \quad \Leftrightarrow \quad -\oint \delta w = \oint \delta q$$

Energy vs. Enthalpy

For a change in state at constant volume, no expansion work is done, so $\Delta U = q_V$, $dU = \delta q_V$

However, for a change in state at constant pressure,

$$\Delta U = q_P + w, \quad dU = \delta q_P - PdV$$

$$\Delta U = \int_1^2 dU = \int_1^2 \delta q_P - \int_{V_1}^{V_2} PdV$$

$$U_2 - U_1 = q_P - P(V_2 - V_1) \quad P \text{ constant}$$

$$(U_2 + PV_2) - (U_1 + PV_1) = q_P$$

$$(U_2 + P_2V_2) - (U_1 + P_1V_1) = q_P \quad P = P_1 = P_2$$

Enthalpy

$$H = U + PV$$

$$\Delta H = q_P, \quad dH = \delta q_P$$

H , being a function of state variables only, is also a state variable.

For a general change of state (P and V may both change),

$$\Delta H = \Delta U + \Delta(PV)$$

$$= \Delta U + P\Delta V + V\Delta P + \Delta P\Delta V$$

$$dH = dU + PdV + VdP$$

Heat Capacity

Transfer of heat to a system *may* result in a rise in T .

$$\delta q = C dT$$

↖ path function, so C depends on conditions.

Define: $\delta q_V = C_V dT$ at constant volume, *no work*

$\delta q_P = C_P dT$ at constant pressure, *only PV work*

From 1st Law, $dU = \delta q + \delta w = \delta q - P_{\text{ex}} dV$

assume no
other work

$$dU = \delta q_V \quad \text{for } dV = 0$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

Similarly

$$dH = dU + PdV + VdP$$

$$= (\delta q - PdV) + PdV + VdP$$

$$= \delta q_P \quad \text{for } dP = 0$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

For ideal gases $dH = dU + d(PV) = dU + nRdT$

$$C_P dT = C_V dT + nRdT$$

$$\bar{C}_P = \bar{C}_V + R$$

The Relation Between C_P and C_V

$$C_P - C_V = \left(\frac{\partial H}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V$$

$$= \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V$$

$H = U + PV$

But since

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

$$\left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

$$\Rightarrow C_P - C_V = \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

work needed to overcome intermolecular forces expansion per degree

$$\left(\frac{\partial U}{\partial V} \right)_T = \text{“internal pressure”}$$

For ideal gases

$$\left(\frac{\partial U}{\partial V} \right)_T = 0, \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} \quad \Rightarrow \quad C_P - C_V = nR$$

For liquids and solids

$$\left(\frac{\partial V}{\partial T} \right)_P \text{ is so small that } C_P \approx C_V$$

Adiabatic Expansion 1

adiabatic = insulated: $q = 0, \quad \delta q = 0$
 $\Delta U = w \quad dU = \delta w$

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

$$w = \int_1^2 dU = \int_{T_1}^{T_2} C_V dT + \dots \quad (0 \text{ for ideal gases})$$
$$= C_V \Delta T \quad \text{if } C_V \text{ is independent of } T$$

For adiabatic expansion $w \leq 0, \quad \Delta U \leq 0 \Rightarrow T_2 \leq T_1$

Free expansion: $P_{\text{ex}} = 0 \Rightarrow w = 0, \quad \Delta T = 0$

Fixed pressure: $w = -P_{\text{ex}} \Delta V$
 $w = \Delta U = C_V \Delta T$
 $\Rightarrow \Delta T = -\frac{P_{\text{ex}} \Delta V}{C_V}$

Reversible expansion: $P = P_{\text{ex}}$
 $w = -\int_{V_1}^{V_2} P(V, T) dV$

Substitute appropriate equation of state. 

Not useful if T changes.

Adiabatic Expansion 2

Reversible adiabatic expansion of ideal gases:

$$dU = \delta w$$

$$\delta q = 0$$

$$C_V dT = -PdV = -\frac{nRT}{V} dV$$

ideal gases only

$$\bar{C}_V \int_1^2 \frac{1}{T} dT = -R \int_1^2 \frac{1}{V} dV$$

$$\begin{aligned} \bar{C}_V \ln(T_2/T_1) &= -R \ln(V_2/V_1) \\ &= -(\bar{C}_P - \bar{C}_V) \ln(V_2/V_1) \end{aligned}$$

$$\ln(T_2/T_1) = -(\gamma - 1) \ln(V_2/V_1)$$

$$\gamma = \frac{\bar{C}_P}{\bar{C}_V}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

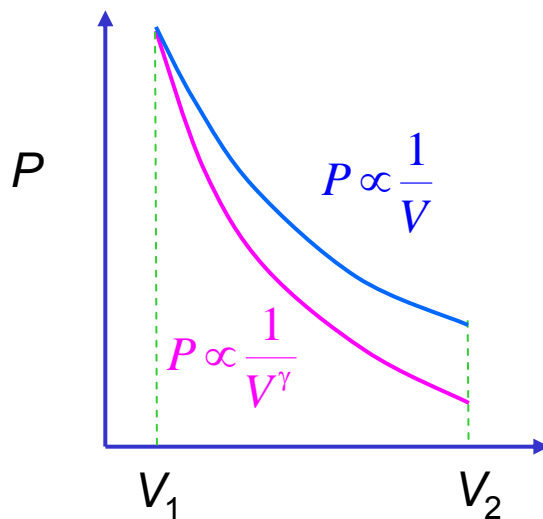
Also, since

$$\frac{P_2 V_2}{P_1 V_1} = \frac{T_2}{T_1}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^\gamma$$

or $P_1 V_1^\gamma = P_2 V_2^\gamma$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma}$$



Types of Expansion Work — Summary

For **all types** of expansion $\delta w = -P_{\text{ex}} dV$

For **reversible** changes $P_{\text{ex}} = P = P(V, T)$ in general

In an **irreversible** expansion $P_{\text{ex}} < P$, $(-w) < (-w_{\text{rev}})$

For **isothermal** expansions T is held constant by leakage of heat into the system from the surroundings.

For an ideal gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$, $\Delta U = 0$, $q = w$

In an **adiabatic** expansion $q = 0$

so the internal energy must provide for the work: $w = \Delta U$

For **reversible expansion of an ideal gas** through a given volume change from the same initial state,

$$(-w_{\text{isothermal}}) > (-w_{\text{adiabatic}})$$

since U is continuously replenished by heat intake to keep the temperature constant.