

Chapter 2. The First Law of Thermodynamics. Heat, Work, Internal Energy, and Enthalpy

Summary

- the **internal energy** U of systems and its significance are discussed
- the First Law of Thermodynamics ($\Delta U = q + w$) is used to relate changes in internal energy to the heat absorbed by a system (q) and the work done on a system (w)
- **enthalpy** $H = U + pV$, heat capacities, and calorimetry are introduced
- **state functions** (*e.g.*, U and H) and **path functions** (*e.g.*, q , w) are distinguished
- ΔU , ΔH , q , and w calculations are illustrated for ideal gases
- differences between **reversible and irreversible processes** are noted

Section 2.1 Internal Energy and the First Law

The internal energy of a system can take many different forms:

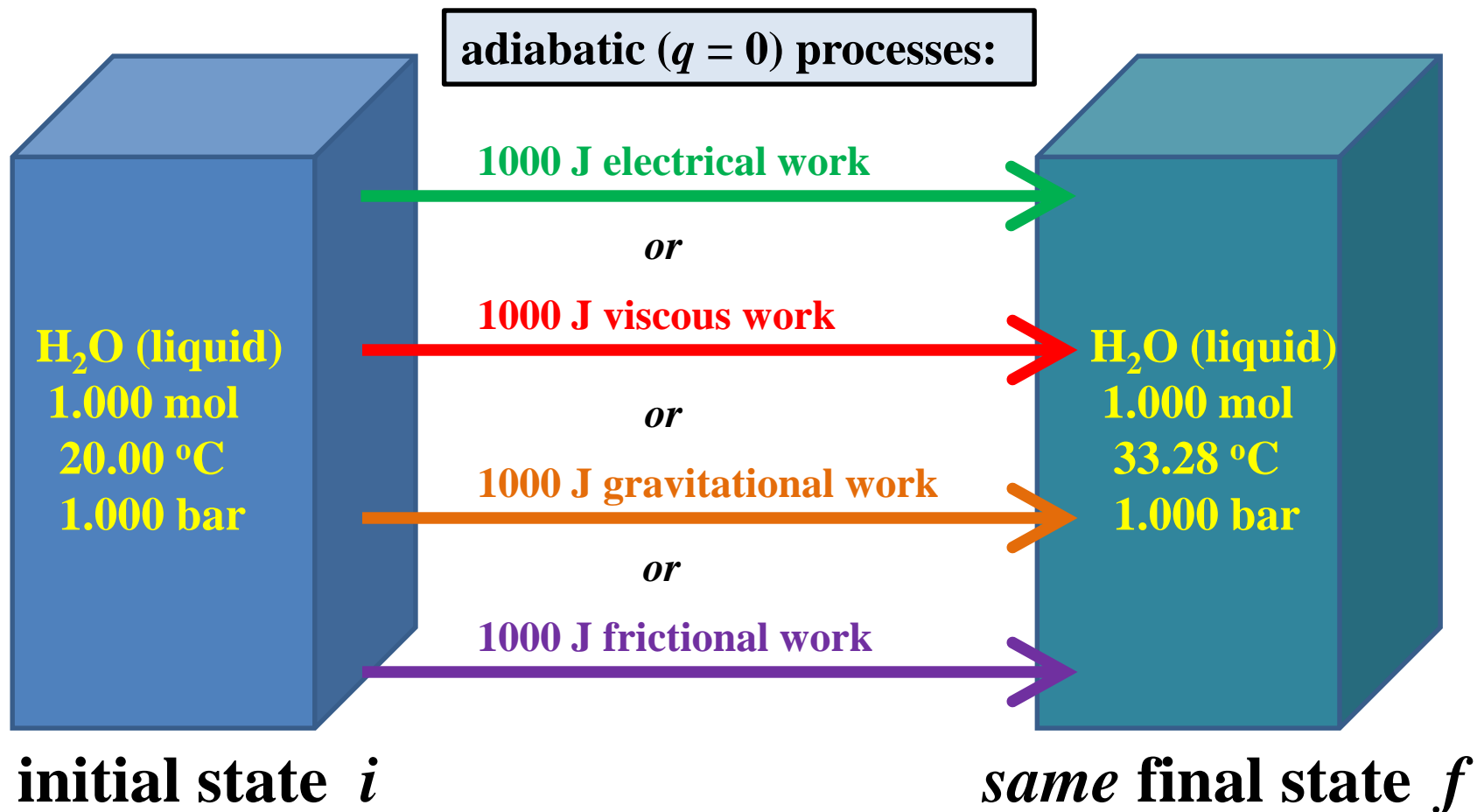
- molecular translational, rotational, vibrational energy
- energy stored in chemical bonds
- potential energy due to interactions between atoms or molecules
- potential energy due to applied electrical, magnetic, or gravitational fields

The **internal** energy **does not include** kinetic energy of a system moving with respect to an **external** coordinate system, such as the kinetic energy of a pizza moving in a delivery vehicle.

Joule's Brilliant Experiment, Leading to the First Law

Before the development of microscopic theory, heat was treated (*incorrectly!*) as a “caloric fluid”, flowing from warmer to cooler objects, leading to much confusion.

For a system in a thermally insulated container (*no confusing heat flow!*) changing from an initial state to a final state, Joule showed that the work done is the same for all processes, *independent of the path connecting the two states*.



The First Law of Thermodynamics

If a system changes from an initial state to a final state, the work done is the same for all adiabatic processes ($q = 0$) connecting the two states.

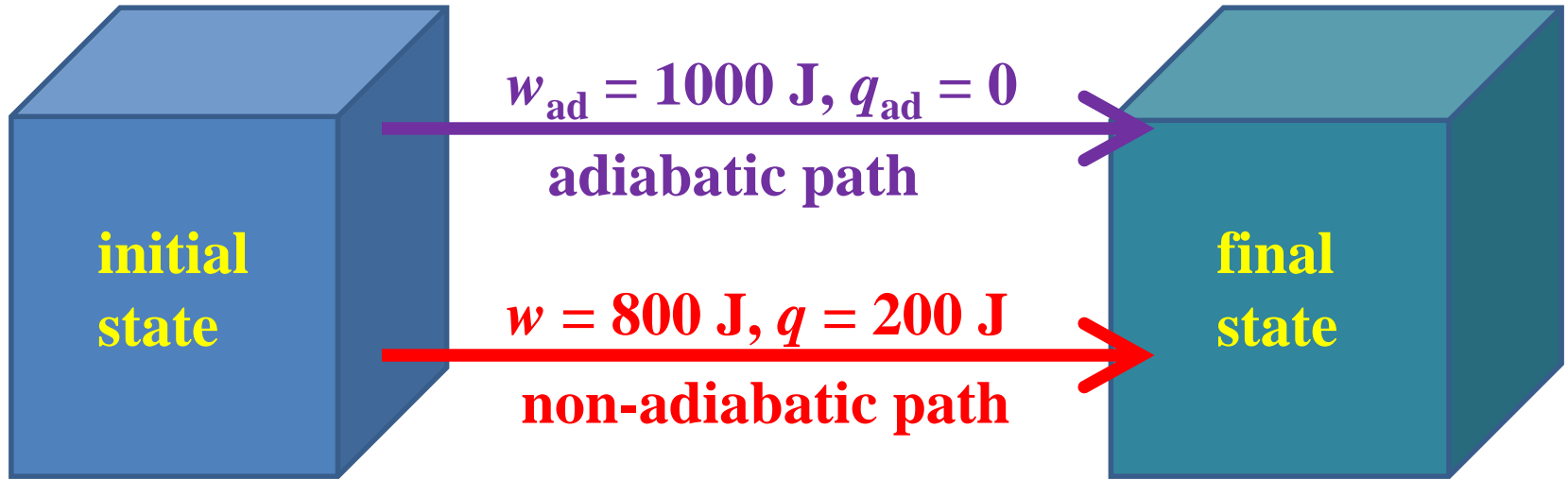
So what? Well, there are important consequences:

I) Because $\Delta U = U_{\text{final}} - U_{\text{initial}} = w_{\text{adiabatic}}$ is independent of the path taken from the initial to the final state of a system, an internal energy function U exists that is a function only of the state variables of systems [e.g., $\Delta U = U(T_f, V_f) - U(T_i, V_i)$].

II) Because U is a function, it can be differentiated and integrated.

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

III) Mechanical definition of heat



$$\Delta U = w_{\text{ad}} = q + w \quad (\text{path-independent})$$

$$q = w_{\text{ad}} - w$$

Allows heat flows to be calculated in terms of well-known mechanical work quantities (a force acting through a distance).

IV) Heat and work are path-dependent, not state functions.

$$\cancel{q(T,V)}$$

$$\cancel{(\partial q/\partial T)_V}$$

$$\cancel{(\partial q/\partial V)_T}$$

$$\cancel{\Delta q = q_f - q_i}$$

$$\cancel{w(T,V)}$$

$$\cancel{(\partial w/\partial T)_V}$$

$$\cancel{(\partial w/\partial V)_T}$$

$$\cancel{\Delta w = w_f - w_i}$$

V) For any **cyclic process** (initial state ... \rightarrow ... same initial state):

$$\oint_i^i dU = 0$$

VI) From $\Delta U = q + w$ it follows that the energy of an isolated system ($q = 0$, $w = 0$) is constant.

$$(\Delta U = 0)_{\text{isolated system}}$$

The energy of the universe (“everything”!) is constant.

\Rightarrow **Conservation of Energy**

Section 2.2 Work

Thermodynamic work w is defined as energy entering a system from the surroundings due to a force \mathbf{F} acting through a distance \mathbf{x} .

$$w = \int_{\mathbf{x}_i}^{\mathbf{x}_f} \mathbf{F} \cdot d\mathbf{x}$$

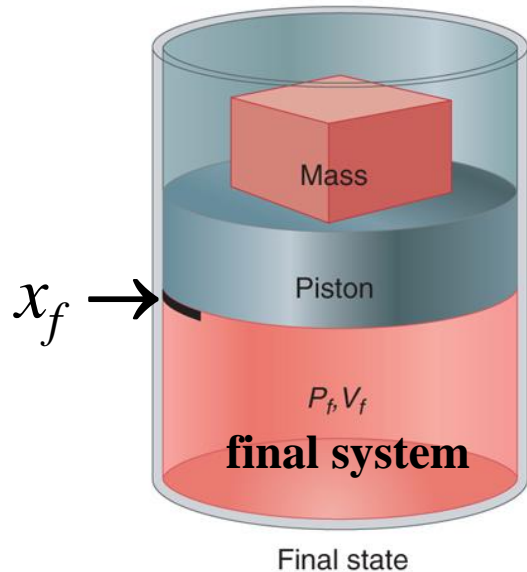
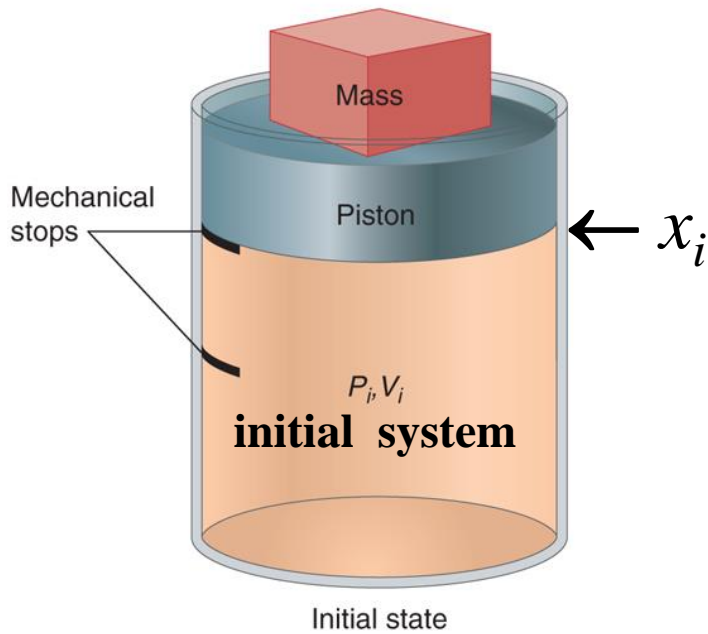
$$\Delta U = q + w$$

if w is positive: the surroundings does work on the system and the internal energy of the system increases

if w is negative: the system does work on the surroundings and the internal energy of the system decreases

!! Warning !! In some treatments of thermodynamics, especially mechanical engineering courses, the opposite convention is used: $\Delta U = q - w$. In this case, w is positive if the system (e.g., an engine) does work on the surroundings.

Volume Expansion Work (also called pV work)



Piston of area A applies force F on the system in the cylinder. The applied force per unit area equals the external pressure acting on the system.

$$w = \int_{x_i}^{x_f} \mathbf{F} \cdot d\mathbf{x} = - \int_{x_i}^{x_f} p_{\text{external}} A dx$$

Why the minus sign? Because vectors \mathbf{F} and $d\mathbf{x}$ point in opposite directions. Note also that $A dx = dV$, the change in volume of the system, which gives

$$w = - \int_{V_i}^{V_f} p_{\text{external}} dV$$

Different Kinds of Thermodynamic Work

TABLE 2.1 Types of Work

Types of Work	Variables	Equation for Work	Conventional Units
Volume expansion	Pressure (P), volume (V)	$w = - \int_{V_i}^{V_f} P_{external} dV$	$\text{Pa m}^3 = \text{J}$
Stretching	Force (F), length (l)	$w = \int_{x_i}^{x_f} \mathbf{F} \cdot d\mathbf{l}$	$\text{N m} = \text{J}$
Surface expansion	Surface tension (γ), area (σ)	$w = \int_{\sigma_i}^{\sigma_f} \gamma \cdot d\sigma$	$(\text{N m}^{-1})(\text{m}^2) = \text{J}$
Electrical	Electrical potential (ϕ), electrical charge (Q)	$w = \int_0^Q \phi dQ'$	$\text{V C} = \text{J}$

SI (*Systeme International d'Unites*) Base Units

length meter (m) from Greek *metros* (measure)

mass kilogram (kg) 1000 grams, from Greek *gramma* (small amount)

time second (s) *second* division of an hour, after minutes

SI Units Named after Scientists

force (mass times acceleration): Newton (N) = kg m s^{-2}

energy (force times distance): Joule (J) = $\text{kg m}^2 \text{s}^{-2}$

pressure (force per unit area): Pascal (Pa) = $\text{kg m}^{-2} \text{s}^{-2}$

temperature Kelvin (K)

Other Units

liter (L) = 0.001 m^3

from French *litron* (a unit of volume)

bar (bar) = $100,000 \text{ Pa}$

from Greek *baros* (weight)

atmosphere (atm) = $101,325 \text{ Pa}$

from Greek *atmos* (vapor) and *sphaira* (sphere)

torr (torr) = $1/760 \text{ atm}$
= $101325/760 \text{ Pa}$

named after **Torricelli** (who developed barometers to measure pressure), the pressure exerted by a 1 mm tall column of liquid mercury

mole (mol) = number of atoms
in 12 grams of ^{12}C

from German *molekul* (molecule)

Exercise

2.00 moles of an ideal gas expands isothermally at 300 K from an initial pressure of 5.00 bar to a final pressure of 2.00 bar.

a) The expansion is carried out rapidly and **irreversibly** with the external pressure suddenly reduced to 2.00 bar: $p_{\text{external}} < p$

b) The expansion is carried out slowly and **reversibly** with the external pressure infinitesimally less than the gas pressure: $p_{\text{external}} = p$

$$V_i = \frac{nRT}{p_i} = \frac{(2.00 \text{ mol})(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{5.00 \text{ bar}} = 9.977 \text{ L}$$

$$V_f = \frac{p_i}{p_f} V_i = \left(\frac{5.00 \text{ bar}}{2.00 \text{ bar}} \right) 9.977 \text{ L} = 24.94 \text{ L}$$

Exercise (cont.)

a) 2.00 moles of an ideal gas at 300 K and 5.00 bar expands isothermally and **irreversibly** against a constant 2.00 bar external pressure to a final pressure of 2.00 bar. Calculate the work.

$$\begin{aligned} w &= - \int_{V_i}^{V_f} p_{\text{external}} dV = - p_{\text{external}} \int_{V_i}^{V_f} dV \\ &= - p_{\text{external}} \int_{V_i}^{V_f} dV = - p_{\text{external}} (V_f - V_i) = - p_{\text{external}} \Delta V \\ &= -(2.00 \text{ bar}) (24.94 \text{ L} - 9.977 \text{ L}) (10^5 \text{ Pa bar}^{-1}) (10^{-3} \text{ m}^3 \text{ L}^{-1}) \end{aligned}$$

Why? p_{external}
is constant.

$$w = -2993 \text{ J}$$

Work is negative for the expanding gas.
Does this make sense?

Exercise (cont.)

b) 2.00 moles of an ideal gas at 300 K and 5.00 bar expands isothermally and **reversibly** to 2.00 bar against a slowly reducing external pressure equal to the gas pressure ($p_{\text{external}} = p$).

$$\begin{aligned}w &= - \int_{V_i}^{V_f} p_{\text{external}} dV = - \int_{V_i}^{V_f} p dV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV \\&= -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \int_{V_i}^{V_f} d \ln V = -nRT \ln(V_f / V_i) \\&= -(2.00 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \ln(24.94 / 9.977)\end{aligned}$$

$$w = -4570 \text{ J}$$

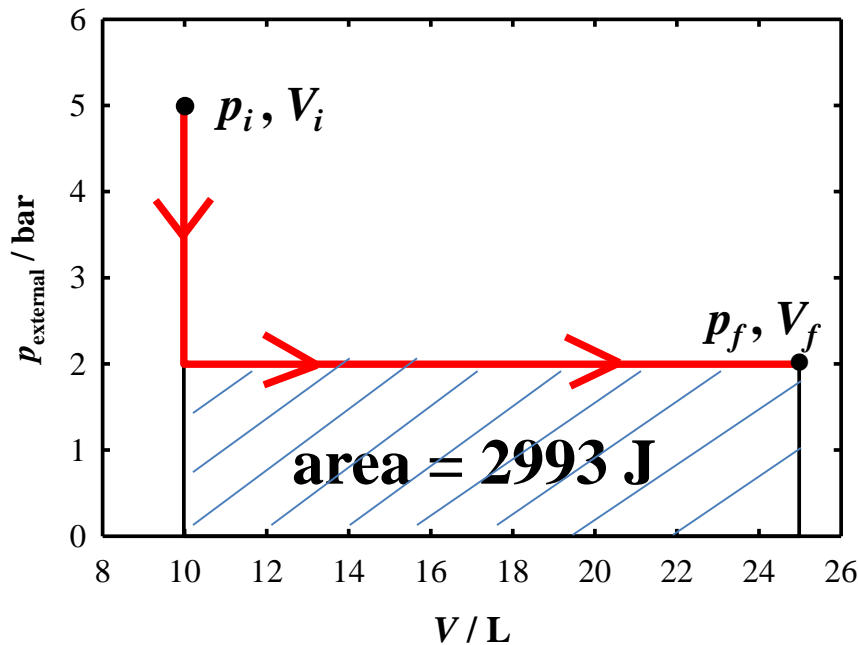
Important! More work is done on the surroundings if the expansion is reversible.

Indicator Diagrams: plot p_{external} against V

Area under the curve is $-w$. Graphical representation of work done.

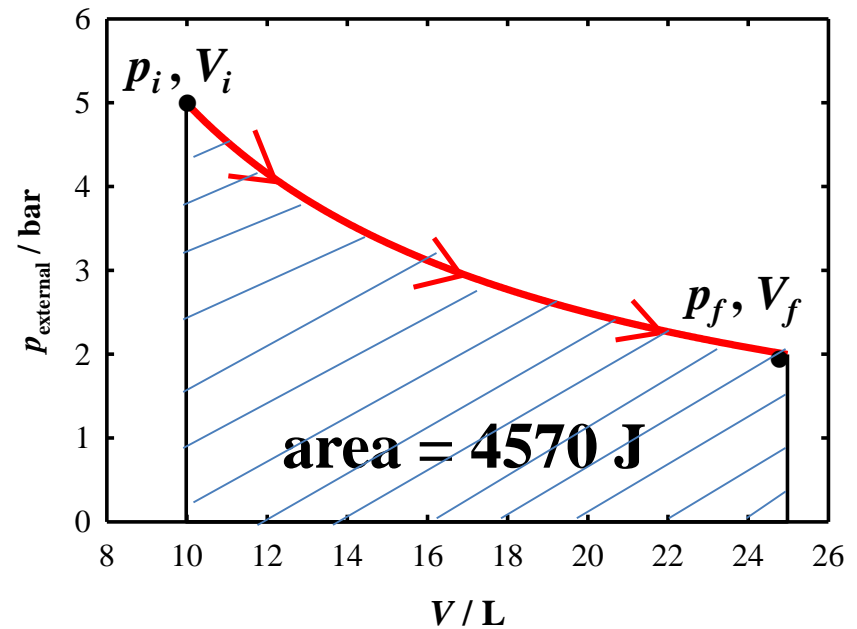
a) Irreversible Expansion

$$p_{\text{external}} = 2 \text{ bar} < p$$
$$w = -2993 \text{ J}$$



b) Reversible Expansion

$$p_{\text{external}} = p$$
$$w = -4570 \text{ J}$$



How do these calculations show that the work is a path function, not a state function?

$$w = - \int_{V_i}^{V_f} p_{\text{external}} dV$$

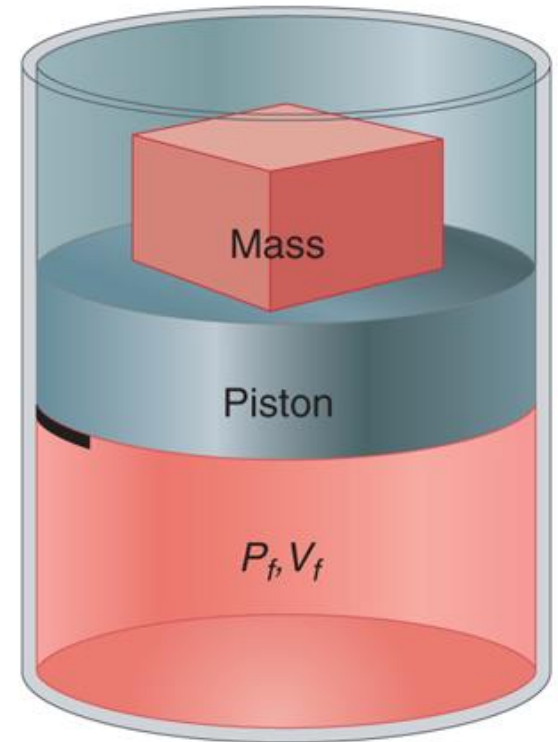
Reversible and Irreversible Expansions

Reversible Expansion: $p_{\text{external}} = p$

The mass holding down the piston is gradually reduced in small increments (*e.g.*, 1 mg). p_{external} is only infinitesimally smaller than the gas pressure p . The gas pressure in the cylinder and the external pressure are balanced. The small mass increments can be replaced, reversing the expansion.

Irreversible Expansion: $p_{\text{external}} < p$

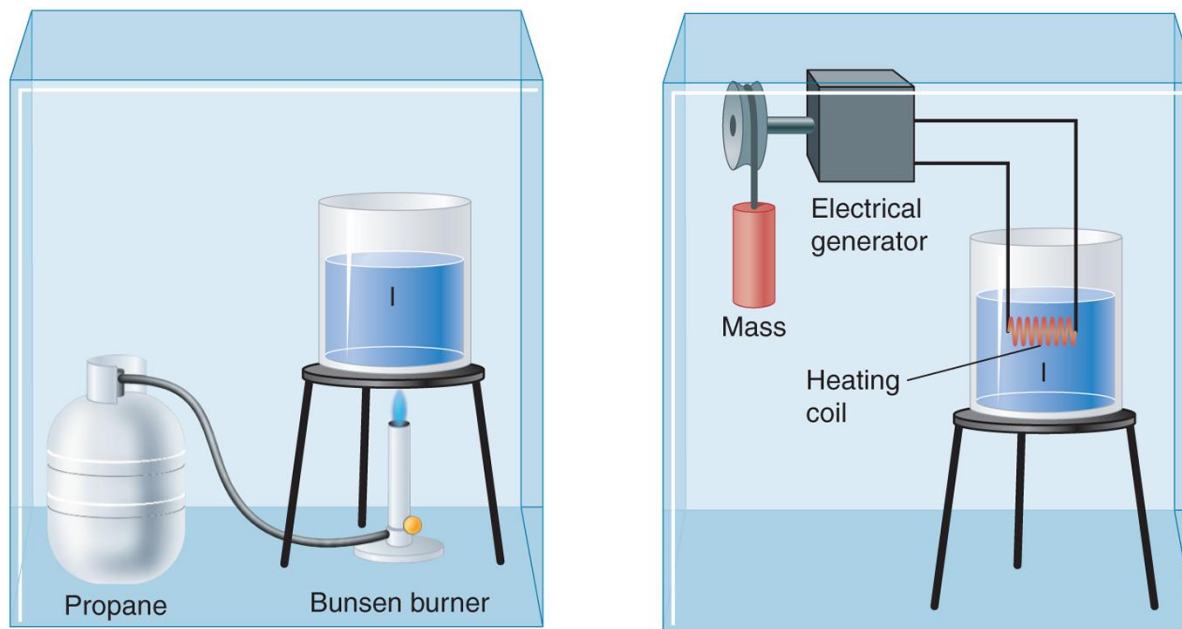
All of the mass holding down the piston is suddenly removed. The gas expands against a lower external pressure. To reverse the process, the mass would have to be lifted to the top of the piston, requiring additional work – *not reversible*.



Sections 2.3-2.5 Heat and Heat Capacity

Heat is defined as energy flowing into a system from the surroundings because of a temperature difference.

Heat flows spontaneously from regions of higher temperature to regions of lower temperature.



Molecular Interpretation of Heat

The internal energy U of a system increases if:

- the system absorbs heat q from the surroundings
- work w is done on the system

$$\Delta U = q + w$$

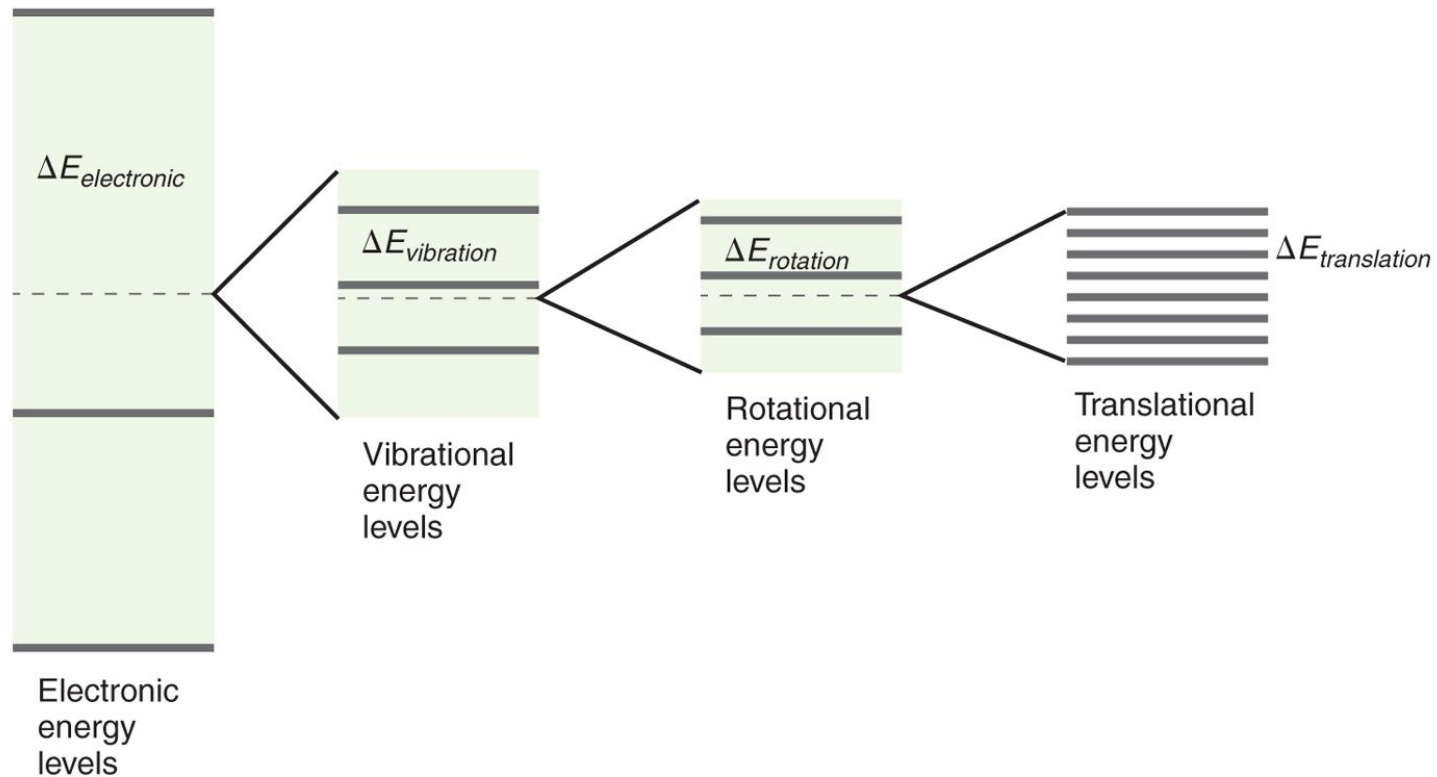
First Law

Work is easily understood in mechanical terms of a force acting through a distance.

But what is heat?

Molecular Energy Levels

Quantum mechanics shows that molecules have electronic, vibrational, rotational, and translational energy levels.



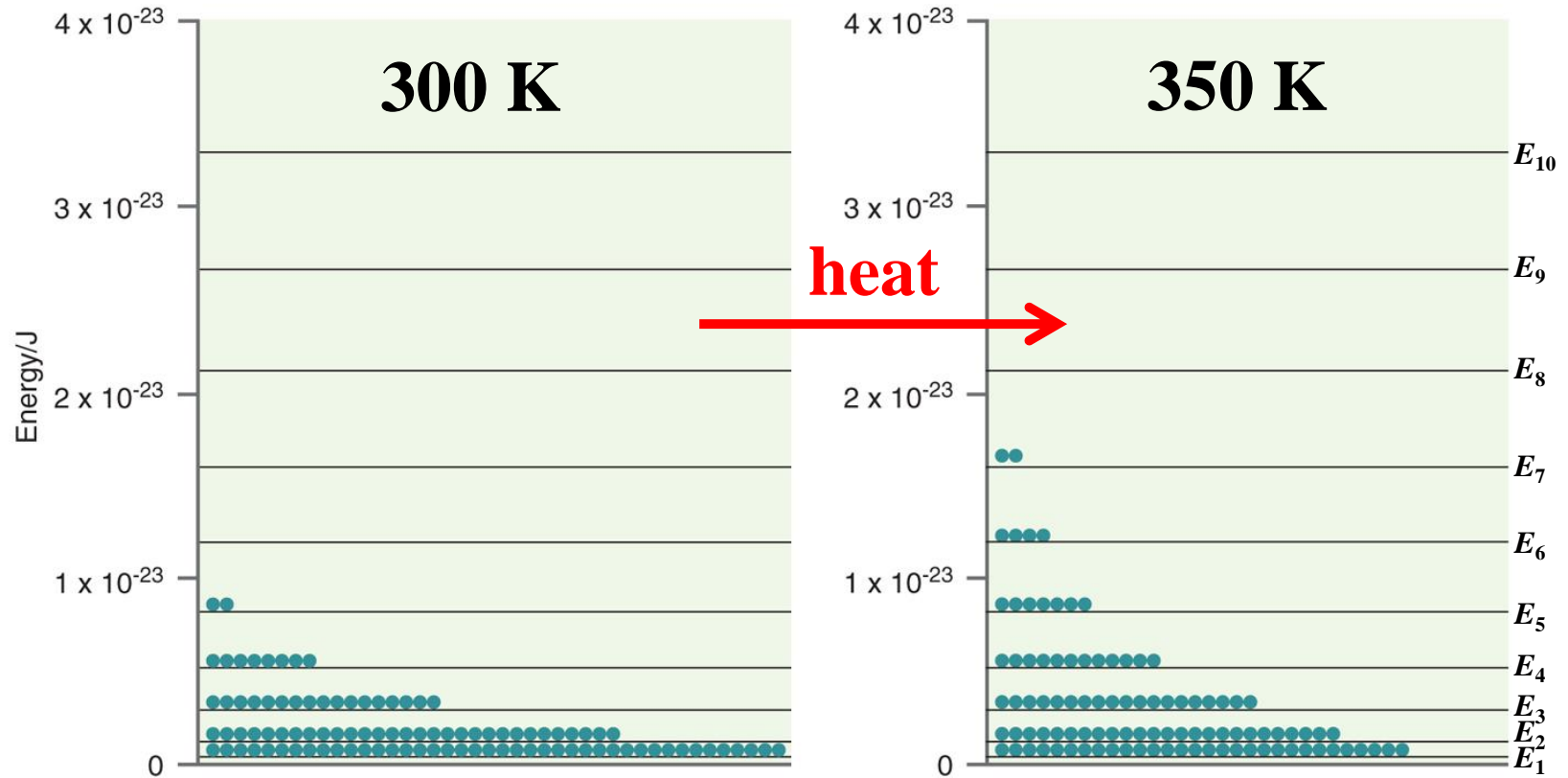
Typical Molecular Energy Level Spacings

TABLE 2.2 Energy Level Spacings for Different Degrees of Freedom

Degree of Freedom	Energy Level Spacing
Electronic	5×10^{-19} J
Vibration	2×10^{-20} J
Rotation	2×10^{-23} J
Translation	2×10^{-41} J



Molecules are Raised to Higher Energy Levels When a System Absorbs Heat



$$\text{Internal Energy } U = \sum_i N_i E_i$$

Heat Capacity C

Add heat q to a system, increasing its temperature by $\Delta T = T_f - T_i$.

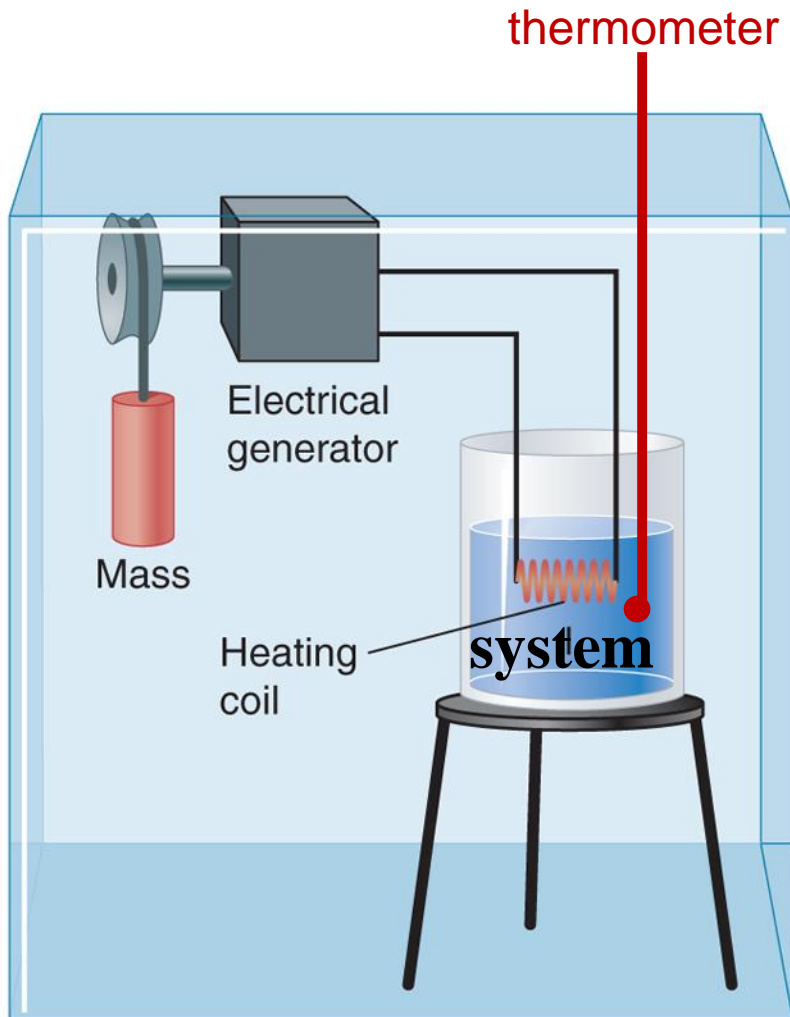
$$C = \lim_{\Delta T \rightarrow 0} \frac{q}{\Delta T}$$

Why take the limit $\Delta T \rightarrow 0$?

C gives the amount of heat required to increase the temperature of a system by 1 K (= 1 °C).

The heat capacity (extensive quantity) increases with the mass of a system and with the number of accessible molecular energy levels.

Heat Capacity Measurements



Embed an electric heater in the system.

Electric current I flowing through voltage difference ϕ for time t delivers heat

$$q = I \phi t$$

to the system. For small temperature changes ($\Delta T \approx 0$):

$$C = \frac{I \phi t}{\Delta T}$$

Heat Capacity at Constant Volume (C_V)

Add heat dq to a system at constant volume ($dV = 0$).

If the only kind of work is p - V work, then

$$\begin{aligned}dU_V &= dq + dw \text{ (First Law)} \\ &= dq_V - p_{\text{external}} dV \\ &= dq_V\end{aligned}$$

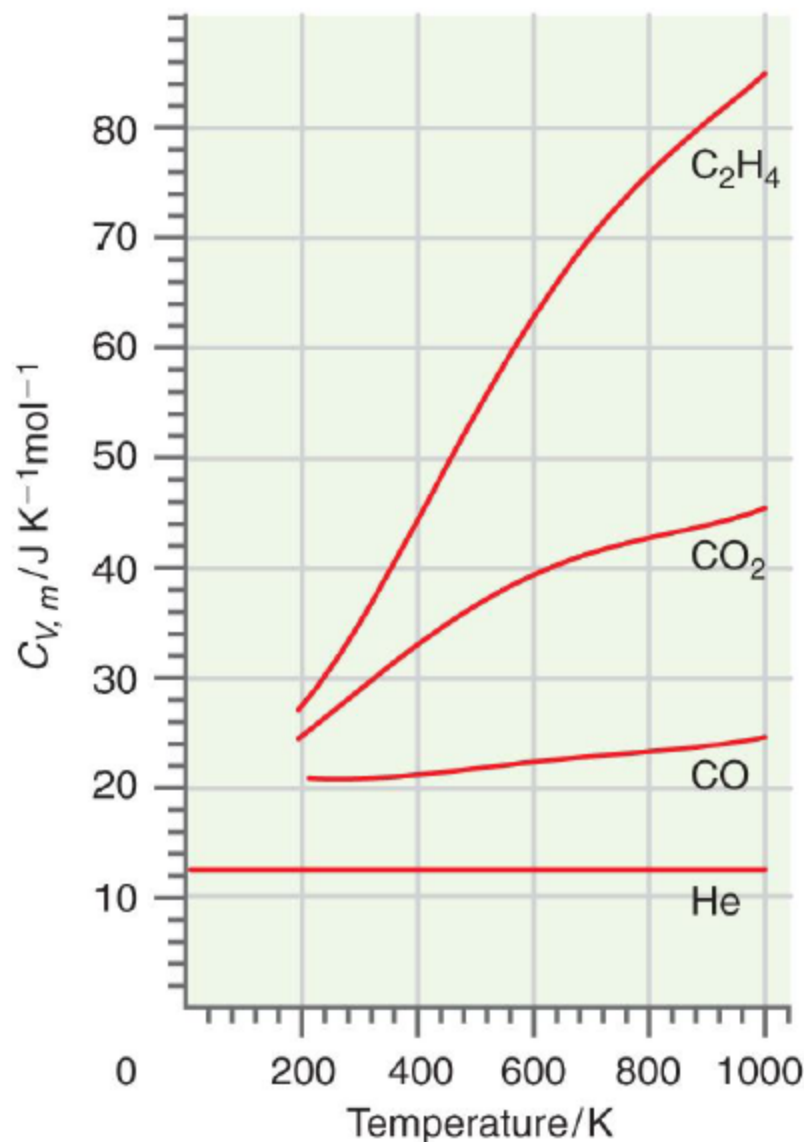
Heat capacity at constant volume:

$$C_V = \frac{dq_V}{dT} = \frac{dU_V}{dT}$$

better notation:

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

Molar Heat Capacities at Constant Volume ($C_{V,m}$) for Gases



For He at low pressures (assuming ideal behavior, *i.e.* no He-He interactions), the energy of one mole of gas is the kinetic energy of the atoms moving in **three dimensions**.

Equipartition Theorem:

Each energy mode contributes $R/2$ to $C_{V,m}$

For He (and other monatomic gases):

$$C_{V,m} = 3(R/2) = 12.5 \text{ J K}^{-1}\text{mol}^{-1}$$

CO, CO₂, C₂H₄, and other polyatomics have translational, rotational, and vibrational energies, and therefore larger heat capacities.

Heat Capacity at Constant Pressure (C_p)

Add heat dq_p to a system at constant pressure ($p = p_{\text{external}}$).

If the only kind of work is p - V work, then $dU = dq + dw$ is

$$\begin{aligned}dU &= dq_p - p_{\text{external}}dV \\ &= dq_p - pdV \\ &= dq_p - d(pV)\end{aligned}$$

Notice $dq_p = dU + d(pV) = d(U + pV)$. Suggests ...

Define the **enthalpy** $H = U + pV$ (a new state function)

$$dq_p = dH_p$$

Heat capacity at constant pressure is

$$C_p = \frac{dq_p}{dT} = \frac{dH_p}{dT}$$

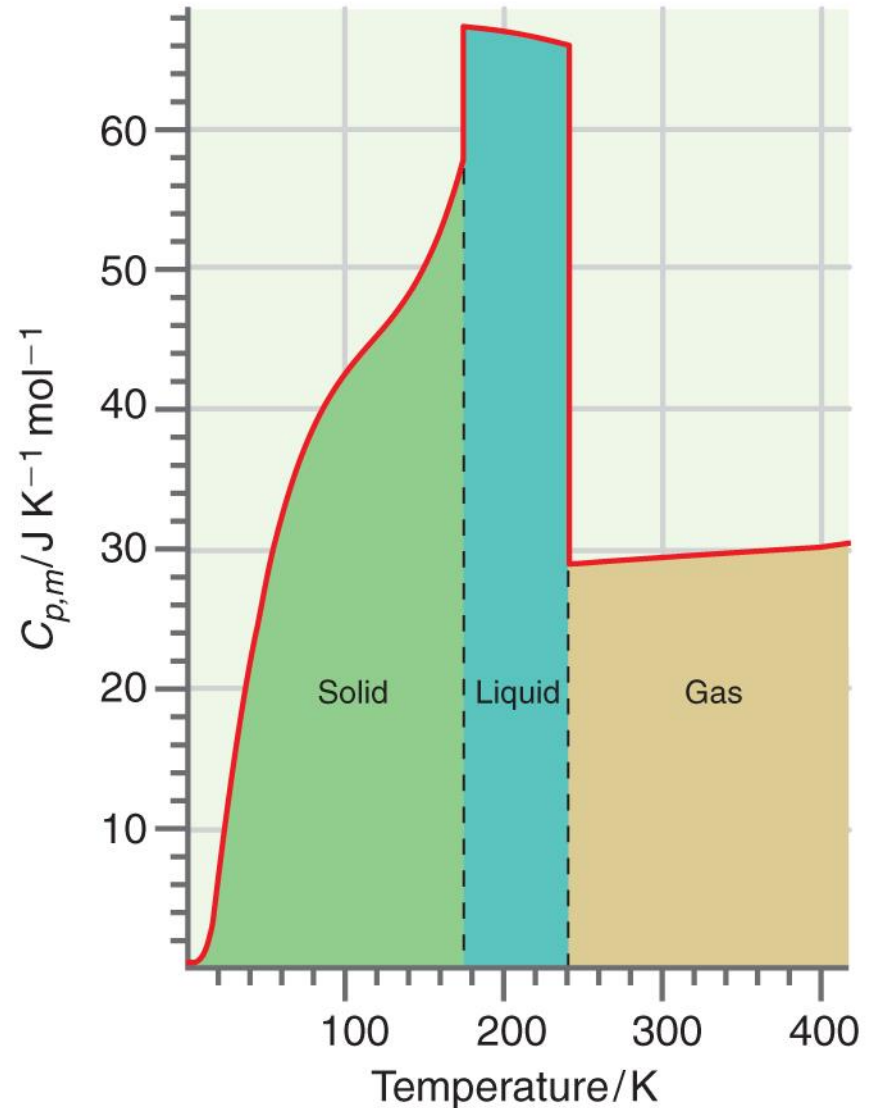
$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

Molar Heat Capacity at Constant Pressure for Cl_2

C_p and C_{pm} are generally easier to measure than C_V and C_{Vm} .

Why?

Solids and liquids heated at constant volume exert enormous pressures on the container walls.



Why Measure Heat Capacities?

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

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

Example A Heat a system at constant volume from temperature T_i to final temperature T_f . The internal energy $U(T, V)$ is a state function. Why not **directly calculate the initial and final internal energy?**

$$\Delta U = U_f(T_f, V) - U_i(T_i, V) = q_V$$

Example B Heat a system at constant pressure from temperature T_i to final temperature T_f . The enthalpy $H(T, p)$ is a state function. Why not **directly calculate the initial and final enthalpy?**

$$\Delta H = H_f(T_f, p) - H_i(T_i, p) = q_p$$

Why Measure Heat Capacities?

Example A Heat a system at constant volume from temperature T_i to final temperature T_f .

$$\Delta U = U_f(T_f, V) - U_i(T_i, V) = q_V$$

Example B Heat a system at constant pressure from temperature T_i to final temperature T_f .

$$\Delta H = H_f(T_f, p) - H_i(T_i, p) = q_p$$

Functions $U(T, V)$ and $H(T, p)$ are known to exist, from the First Law.

But there's a big problem :

Except for very simple systems, such as ideal gases,
the state functions $U(T, V)$ and $H(T, p)$ are unknown!

What to do?

Example A

Heat a system at constant volume from temperature T_i to final temperature T_f .

$$\Delta U = U_f(T_f, V) - U_i(T_i, V) = q_V$$

Absolute internal energies $U_f(T_f, V)$ and $U_i(T_i, V)$ are unknown.

But: $C_V = \left(\frac{\partial U}{\partial T} \right)_V$ multiply both sides by dT

$C_V dT_V = dU_V$ integrate at constant volume

$$\int_{T_i}^{T_f} C_V dT = \int_{U_i}^{U_f} dU_V = U(T_f, V) - U(T_i, V) = \Delta U_V$$

Can use C_V data to calculate the change in the internal energy.

What to do?

Example B

Heat a system at constant pressure from temperature T_i to final temperature T_f .

$$\Delta H = H_f(T_f, p) - H_i(T_i, p) = q_p$$

Absolute enthalpies $H_f(T_f, p)$ and $H_i(T_i, p)$ are unknown.

But: $C_p = \left(\frac{\partial H}{\partial T} \right)_p$ multiply both sides by dT

$C_p dT_p = dH_p$ integrate at constant pressure

$$\int_{T_i}^{T_f} C_p dT = \int_{H_i}^{H_f} dH_p = H(T_f, p) - H(T_i, p) = \Delta H_p$$

Can use C_p data to calculate the change in the enthalpy.

Relation Between C_V and C_p

First Law (at constant pressure): $dU = dq + dw = dq_p - pdV$

$U(V, T)$ is a function that can be differentiated.

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

Divide by dT at constant pressure to get

$$\left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT_p} + \left(\frac{\partial U}{\partial T}\right)_V \frac{dT}{dT_p} = \frac{dq_p}{dT_p} - p \frac{dV}{dT_p}$$

$\left(\frac{\partial V}{\partial T}\right)_p$ C_V 1 C_p $\left(\frac{\partial V}{\partial T}\right)_p$

Relation Between C_V and C_p (*cont.*)

$$\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + C_V = C_p - p \left(\frac{\partial V}{\partial T}\right)_p$$

Rearranges to

$$C_p - C_V = \left[p + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_p$$

Application: Measure C_p , then use the equation for $C_p - C_V$ to calculate C_V (difficult to measure for gases and solids).

Relation Between C_V and C_p (*cont.*)

Use the thermodynamic equation of state $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$

to get

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

Significance: The heat capacity difference $C_p - C_V$ for any system can be calculated from p - V - T data or from equations of state (calorimetry not required)

Exercise: Evaluate $C_p - C_V$ for Ideal Gases ($pV = nRT$)

For ideal gases, recall from Chapter 1 that $(\partial U/\partial V)_T = 0$. *Proof:*

$$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T &= T \left(\frac{\partial p}{\partial T}\right)_V - p \\ &= T \left(\frac{\partial [nRT/V]}{\partial T}\right)_V - p \\ &= T \frac{nR}{V} \left(\frac{\partial T}{\partial T}\right)_V - p \\ &= T \frac{nR}{V} (1) - p = p - p = 0\end{aligned}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

Important The internal energy of an ideal gas depends only on the temperature.

Exercise: Evaluate $C_p - C_V$ for Ideal Gases (*cont.*)

$$\begin{aligned}C_p - C_V &= \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p \\ &= p \left(\frac{\partial V}{\partial T} \right)_p \\ &= p \left(\frac{\partial [nRT / p]}{\partial T} \right)_p \\ &= \cancel{p} \frac{nR}{\cancel{p}} \left(\frac{\partial T}{\partial T} \right)_p\end{aligned}$$

n, R, p are constant

$$C_p - C_V = nR$$

divide by n :

$$C_{pm} - C_{Vm} = R$$

per mole of gas

- Why is C_p larger than C_V ?

Section 2.6 State Functions and Path Functions

- internal energy U and enthalpy H are **state functions** (also called **point functions**)
- state functions depend only on the state variables of systems, such as T , V , composition
- the change in a state function is identical for any process connecting two states of a system
- work w and heat q are **path-dependent** (not state functions or functions)
- different values of q and w are obtained for different processes connecting two states of a system

Mathematical Test for a State Function

Given

$$df = g(x, y)dx + h(x, y)dy$$

the state function $f(x,y)$ exists only if

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

the “test”

Why? If the function $f(x,y)$ exists, then f can be differentiated

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = g(x, y)dx + h(x, y)dy$$

$$g(x, y) = \left(\frac{\partial f}{\partial x}\right)_y \quad h(x, y) = \left(\frac{\partial f}{\partial y}\right)_x$$

Because the order of second partial differentiation doesn't matter:

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

(∂x first then ∂y) (∂y first then ∂x)

Exercise: For the function $f(x,y) = 6x^2y^3$, prove

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

Left Side (∂x first then ∂y):

$$\begin{aligned} \left[\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_y \right]_x &= \left[\frac{\partial}{\partial y} \left(\frac{\partial [6x^2y^3]}{\partial x} \right)_y \right]_x = \left[\frac{\partial}{\partial y} (6 \cdot 2x \cdot y^3) \right]_x = 6 \cdot 2x \cdot 3y^2 \\ &= 36xy^2 \end{aligned}$$

Right Side (∂y first then ∂x):

$$\begin{aligned} \left[\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right)_x \right]_y &= \left[\frac{\partial}{\partial x} \left(\frac{\partial [6x^2y^3]}{\partial y} \right)_x \right]_y = \left[\frac{\partial}{\partial x} (6x^2 \cdot 3 \cdot y^2) \right]_x = 12x \cdot 3y^2 \\ &= 36xy^2 \end{aligned}$$

Exercise: Show that C_V is constant for an isothermal (fixed T) ideal gas.

$$\begin{aligned} \left(\frac{\partial C_V}{\partial V} \right)_T &= \left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T} \right)_V \right]_T && \text{reverse the order of} \\ & && \text{differentiation} \\ &= \left[\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T \right]_V \\ &= \left(\frac{\partial(0)}{\partial T} \right)_V = 0 && \mathbf{0 \text{ for an ideal gas}} \end{aligned}$$

$$\boxed{\left(\frac{\partial C_V}{\partial V} \right)_T = 0}$$

Exercise: Show that the state function $q(T,V)$ does not exist for an ideal gas.

$$dU = dq + dw \quad \text{First Law}$$

The internal energy of an ideal gas ($dU = C_V dT$) depends only on T .

$$C_V dT = dq + dw = dq - pdV$$

Rearranges to $dq = C_V dT + pdV$

Test: $q(T,V)$ exists if $(\partial C_V / \partial V)_T$ and $(\partial p / \partial T)_V$ are identical.

But for an ideal gas, $(\partial C_V / \partial V)_T = 0$ (previous slide) and

$$\left(\frac{\partial p}{\partial T} \right)_V = \left[\frac{\partial(nRT/V)}{\partial T} \right]_V = \frac{nR}{V} \left(\frac{\partial T}{\partial T} \right)_V = \frac{nR}{V} \neq 0$$

Conclusion: the state function $q(T,V)$ does not exist for an ideal gas.

Sections 2.7 to 2.11. Expansion and Compression of Ideal Gases

Why studied?

- important for the design and operation of engines, turbines, compressors, rockets, ...
- refrigeration and heat pumps
- meteorology (*e.g.*, rising air cools, sinking air warms up) and fluid mechanics
- understanding sound waves, shock waves, ballistics, explosions, ...
- useful application of thermodynamic calculations

Application: Steam Turbines



- heat is produced by burning coal, oil, natural gas, or by nuclear fission of uranium
- the heat is used to boil water, producing high-pressure steam
- the expanding steam spins the blades of a turbine
- the rotating turbine shaft runs a generator to produce electricity

Ideal Gas Internal Energy Calculations.

$$dU = C_V dT$$

Integrated $\Delta U = \int_{T_i}^{T_f} C_V dT$ Constant or variable volume.
Reversible or irreversible processes. *Why?*

Constant C_V $\Delta U = C_V \int_{T_i}^{T_f} dT = C_V (T_f - T_i)$

Enthalpy ($H = U + pV$) Calculations.

$$dH = C_p dT$$

Integrated $\Delta H = \int_{T_i}^{T_f} C_p dT$ Constant or variable pressure.
Reversible or irreversible processes. *Why?*

Constant C_p $\Delta H = C_p \int_{T_i}^{T_f} dT = C_p (T_f - T_i)$

Work Calculations.

$$dw = -p_{\text{external}}dV$$

Integrated

$$w = -\int_{V_i}^{V_f} p_{\text{external}}dV$$

Constant p_{external}

$$w = -p_{\text{external}} \int_{V_i}^{V_f} dV = -p_{\text{external}}(V_f - V_i)$$

Reversible process

($p_{\text{external}} = p$)

$$w = -\int_{V_i}^{V_f} pdV = -\int_{V_i}^{V_f} \frac{nRT}{V} dV$$

Reversible process

(constant T)

$$w = -nRT \int_{V_i}^{V_f} \frac{1}{V} dV = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

Reversible process

(constant p)

$$w = -p \int_{V_i}^{V_f} dV = -p(V_f - V_i) = -nR(T_f - T_i)$$

Heat Calculations. q

Calculate w and ΔU , then use the First law to calculate

$$q = \Delta U - w$$

Add heat at constant volume ($w = 0$):

$$q_V = \Delta U$$

Add heat at constant pressure:

$$q_p = \Delta H$$

Adiabatic processes: $q = 0$

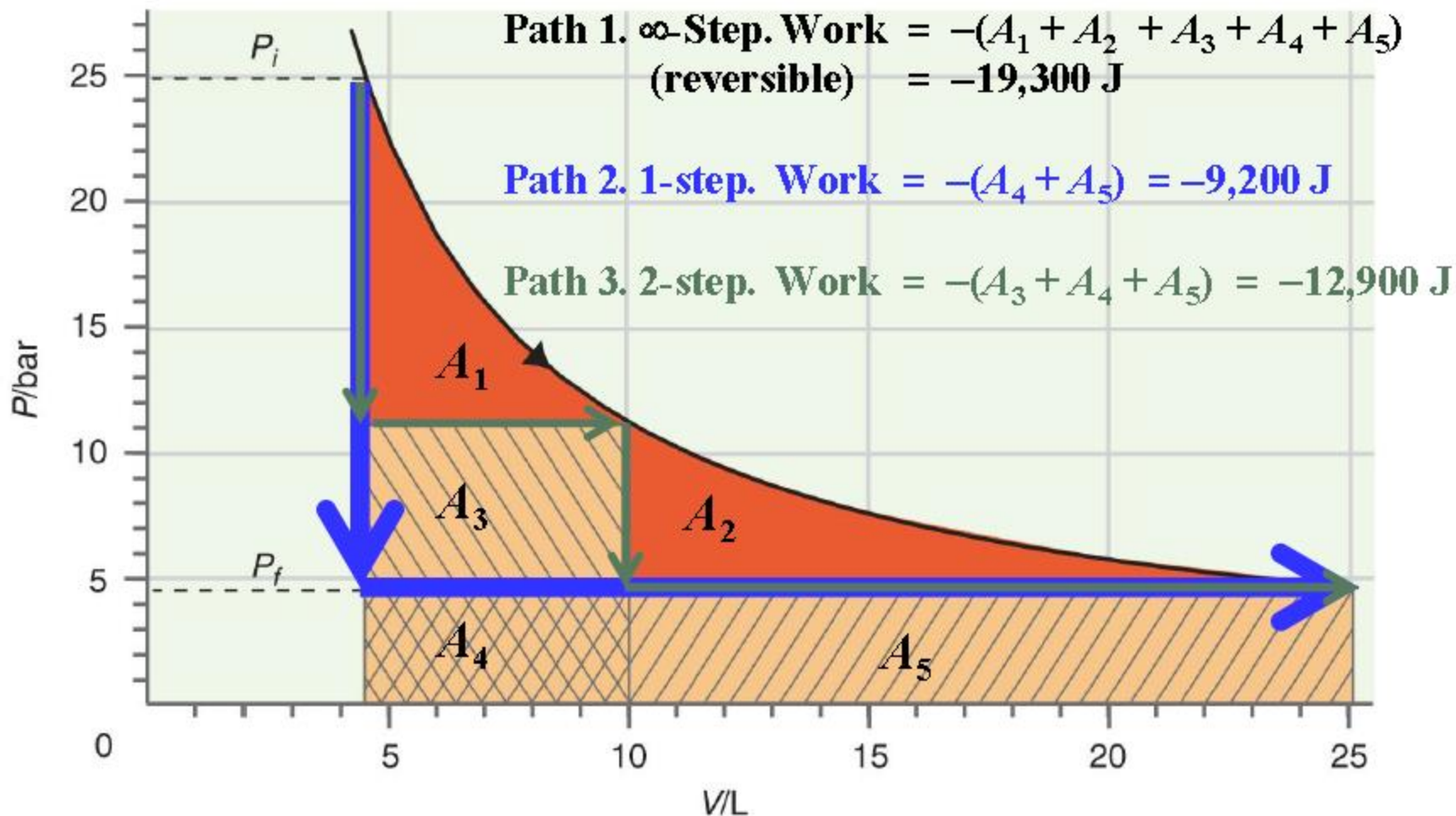
Why are $\Delta q = q_f - q_i$ and $\Delta w = w_f - w_i$ **never used** ?

Example Problem 2.4

2.00 mol of ideal gas expands isothermally along **three different paths**:

- 1) A **reversible expansion** from $p_i = 25.0$ bar and $V_i = 4.50$ L to $p_f = 4.50$ bar.
- 2) A **single-step irreversible expansion** against a constant external pressure of 4.50 bar.
- 3) A **two-step irreversible expansion** against a constant external pressure of 11.0 bar to a gas pressure of 11.0 bar followed by a second irreversible expansion against a constant external pressure of 4.50 bar until $p_f = 4.50$ bar.

Example Problem 2.4 (cont.)



Example Problem 2.4 (cont.)

Work done by the isothermal expansion of 2.00 mol of ideal gas from 25.0 bar and 4.50 L to 4.50 bar and 25.0 L

Path	work w	work done on surroundings $-w$
1-step irrev. $(p_{\text{ext}} < p)$	$-9,200 \text{ J}$	$9,200 \text{ J}$
\vdots	\vdots	\vdots
2-step irrev. $(p_{\text{ext}} < p)$	$-12,900 \text{ J}$	$12,900 \text{ J}$
∞ -step rev. $(p_{\text{ext}} = p = nRT/V)$	$-19,300 \text{ J}$	$19,300 \text{ J}$

Important result: Reversible (quasi-static) expansion does maximum work on the surroundings

Comparison of Reversible (∞ -step) and Irreversible Processes

Expansions

$$(w < 0)$$

$$w_{\text{rev}} < w_{\text{irrev}}$$

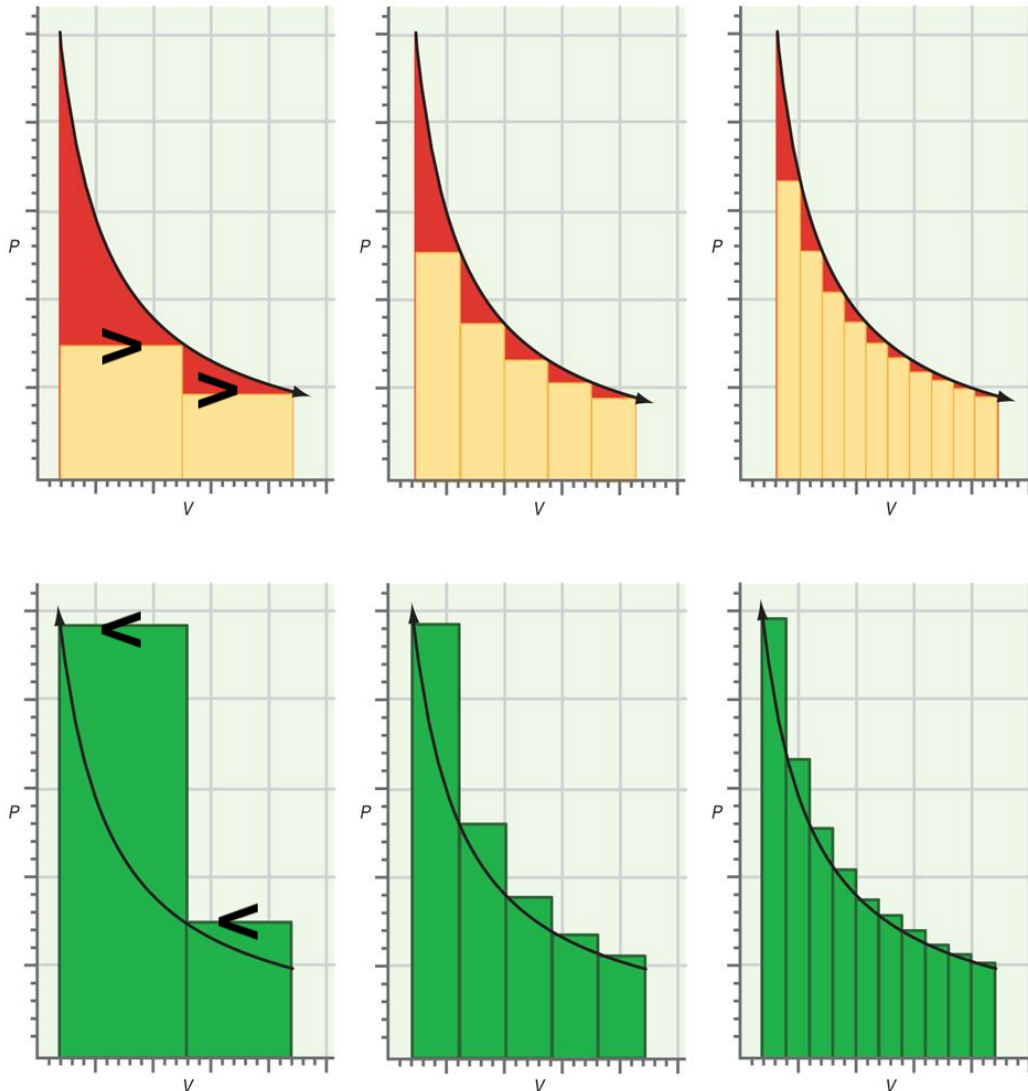
More work done on the surroundings for a reversible expansion.

Compressions

$$(w > 0)$$

$$w_{\text{rev}} < w_{\text{irrev}}$$

Less work required for a reversible compression.



Adiabatic ($q = 0$) Expansions and Compressions

- no heat flow in to or out of a system
- applies to processes for insulated systems and to “fast” processes (no time for heat conduction)
- important examples: explosions, shock waves, sound waves, and power-generating steps in engine cycles

$$dU = \cancel{dq} + dw = dw = -p_{\text{external}}dV$$

For ideal gases (U depends only on T , $dU = C_V dT$), get:

$$C_V dT = -p_{\text{external}} dV$$

$$\int_{T_i}^{T_f} C_V dT = - \int_{V_i}^{V_f} p_{\text{external}} dV$$

Reversible Adiabatic Expansion or Compression of an Ideal Gas

reversible: $p_{\text{external}} = p$

$$C_V dT = -p_{\text{external}} dV = -p dV = -\frac{nRT}{V} dV$$

$$C_V \frac{dT}{T} = -nR \frac{dV}{V}$$

$$\int_{T_i}^{T_f} C_V \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

Tricky to integrate! C_V , T , V are all changing!

But if the heat capacity C_V is constant, ...

Reversible Adiabatic Expansion or Compression of an Ideal Gas Constant C_V

$$\int_{T_i}^{T_f} C_V \frac{dT}{T} = C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i} \quad \text{use } C_{V_m} = C_V/n \text{ to get:}$$

$$C_{V_m} \ln \frac{T_f}{T_i} = -R \ln \frac{V_f}{V_i}$$

- constant C_{V_m}
- ideal gas
- valid for monatomic gases and polyatomics over small temperature ranges (then C_{V_m} is “almost” constant)

Exercise: Air, initially at 25 °C, is compressed adiabatically by a factor of 9 (= compression factor V_i/V_f).
Estimate the final temperature T_f .

N_2 and O_2 molecules have three translational modes and two rotational modes of kinetic energy, each contributing $R/2$ to $C_{V,m}$.

Data:

$$C_{V,m} = 3(R/2)_{\text{trans}} + 2(R/2)_{\text{rot}} = 5(R/2)$$
$$T_i = (25 + 273.15) \text{ K} = 298.15 \text{ K}$$
$$V_f/V_i = 1/9$$

Use:

$$C_{V,m} \ln \frac{T_f}{T_i} = -R \ln \frac{V_f}{V_i}$$

$$\frac{5}{2} R \ln \frac{T_f}{298.15 \text{ K}} = -R \ln \frac{1}{9}$$

(assumes compression is reversible and $C_{V,m}$ is constant)

solve for:

$$T_f = 718 \text{ K} \text{ (445 °C)}$$

!!! HHHot !!!

Application: Diesel engines (reliable and efficient) don't need spark plugs.

No heat is added to adiabatically compressed systems, but they can get **very hot**.

No heat is lost from adiabatically expanded systems, but they can get **very cold**.

Make sure you know why!

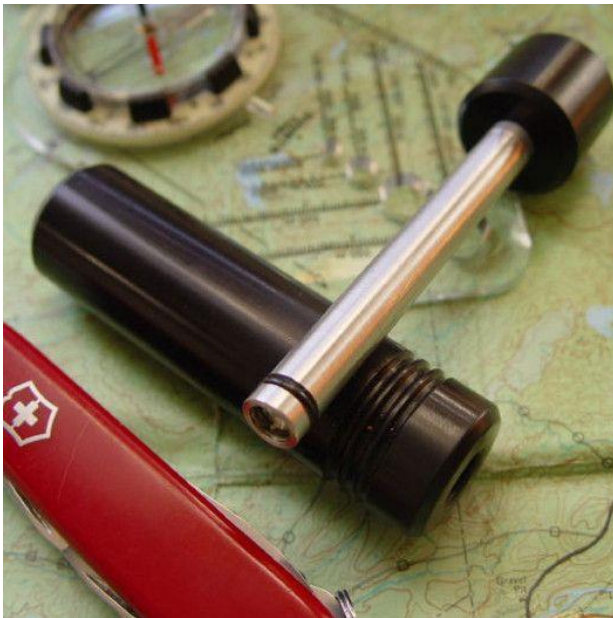


Fire Piston

Fuel and air in a cylinder adiabatically compressed by a piston get hot, reach ignition temperature.

Used for hundreds of years to start fires for heat and cooking (without matches).

Inspired Rudolph Diesel to invent the diesel engine in the 1890s.



Slam-Rod™ Fire Starter

No matches, no rubbing sticks together, no flint, no electricity, and re-usable.

(USD 22.75 from Amazon, plus shipping and taxes)

What's causing the white cloud? Is it smoke? A fire?



Sounds and music we hear are waves of adiabatic compression and expansion moving through air.

Why adiabatic? Why not isothermal?



Fast (Adiabatic) Compressions and Expansions

sound waves, hearing, music, ... *but also*:

- ◆ **ultrasonic imaging** without electromagnetic radiation
- ◆ **sonar** for sound echo location and mapping (bats do it too!)
- ◆ **hydrophones** for long-range passive listening and detection
- ◆ **SOSUS** (ocean **SO**und **SU**rveillance **S**ystem)
- ◆ **seismology** studies of earthquakes the interior of the earth
- ◆ **seismic mapping** of petroleum and natural gas deposits
- ◆ **sonochemistry** (chemical reactions produced by sound waves)
- ◆ **shock wave** studies of matter under extreme conditions

Reversible Adiabatic Expansion or Compression of an Ideal Gas

Constant C_{V_m} (another useful result)

$$C_{V_m} \ln \frac{T_f}{T_i} = -R \ln \frac{V_f}{V_i}$$

recall $C_{V_m} + R = C_{p_m}$

$$C_{V_m} \ln \left(\frac{T_f}{T_i} \right) = C_{V_m} \ln \left(\frac{\frac{p_f V_f}{nR}}{\frac{p_i V_i}{nR}} \right) = C_{V_m} \ln \left(\frac{p_f V_f}{p_i V_i} \right) = -R \ln \frac{V_f}{V_i}$$

$$C_{V_m} \ln \frac{p_f}{p_i} = -C_{V_m} \ln \frac{V_f}{V_i} - R \ln \frac{V_f}{V_i} = -C_{p_m} \ln \frac{V_f}{V_i} = C_{p_m} \ln \frac{V_i}{V_f}$$

$$\ln \frac{p_f}{p_i} = \frac{C_{p_m}}{C_{V_m}} \ln \frac{V_i}{V_f} = \ln \left(\frac{V_i}{V_f} \right)^{C_{p_m}/C_{V_m}} \quad \frac{p_f}{p_i} = \left(\frac{V_i}{V_f} \right)^{C_{p_m}/C_{V_m}}$$

Often written as:

$$p_i V_i^\gamma = p_f V_f^\gamma \quad \text{with} \quad \gamma = C_{p_m}/C_{V_m}$$

Isotherms (fixed T) and Adiabats ($q = 0$) for an Ideal Gas

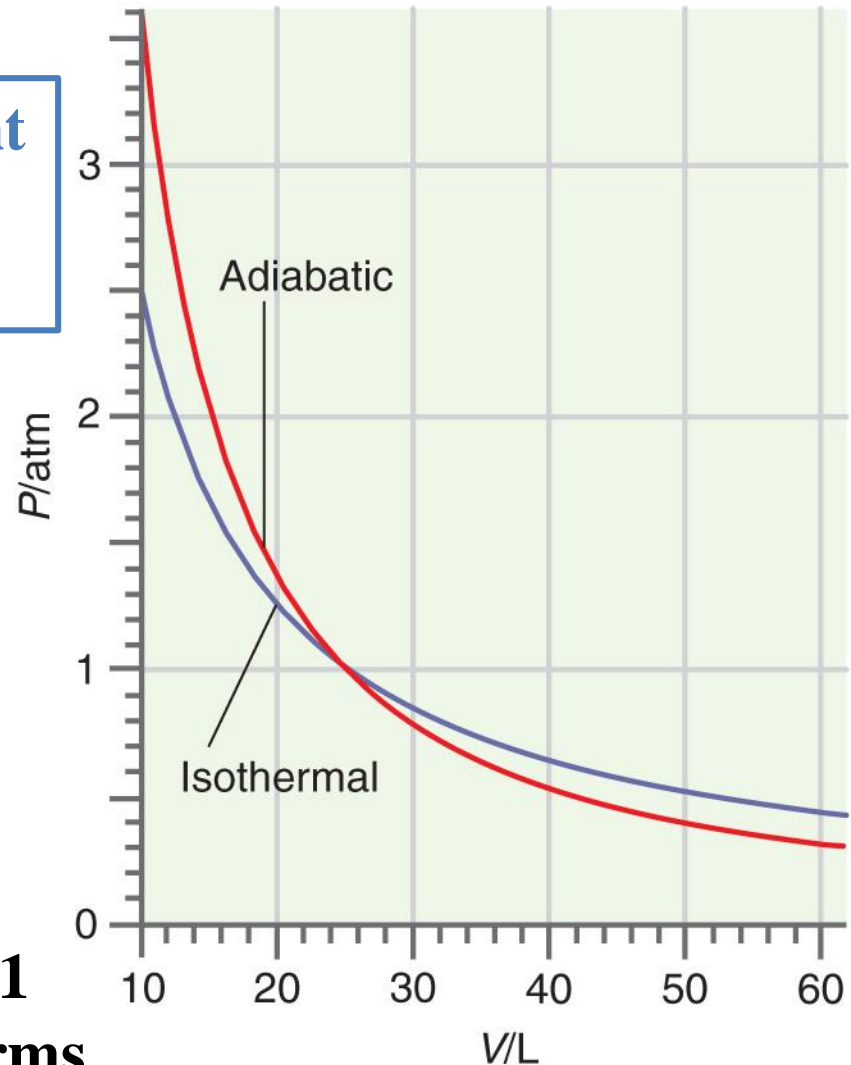
Isotherms: $pV = nRT = \text{constant}$

$$\text{slope} = (\partial p / \partial V)_T = -p/V$$

Adiabats: $pV^\gamma = \text{constant}$

$$\text{slope} = (\partial p / \partial V)_{q=0} = -\gamma p/V$$

$\gamma = C_p / C_V = (C_{Vm} + R) / C_{Vm} > 1$
adiabats are steeper than isotherms



Isotherm Slopes (Ideal Gas)

$$pV = nRT = \text{constant}$$

$$d(pV) = d(\text{constant}) = 0$$

$$pdV + Vdp = 0 \quad \div dV_T$$

$$p + V\left(\frac{\partial p}{\partial V}\right)_T = 0$$

$$\boxed{\left(\frac{\partial p}{\partial V}\right)_T = -\frac{p}{V}}$$

Adiabat Slopes (Ideal Gas, γ constant)

$$pV^\gamma = \text{constant}$$

$$d(pV^\gamma) = d(\text{constant}) = 0$$

$$pdV^\gamma + V^\gamma dp = 0$$

$$p\gamma V^{\gamma-1} dV + V^\gamma dp = 0 \quad \div dV_{q=0}$$

$$p\gamma V^{\gamma-1} + V^\gamma \left(\frac{\partial p}{\partial V} \right)_{q=0} = 0$$

$$\boxed{\left(\frac{\partial p}{\partial V} \right)_{q=0} = -\gamma \frac{p}{V}}$$

Significance *Isotherm slopes and adiabat slopes differ by a factor of γ . Will be useful later!*