Thermochemistry 2:
First Law of Thermodynamics

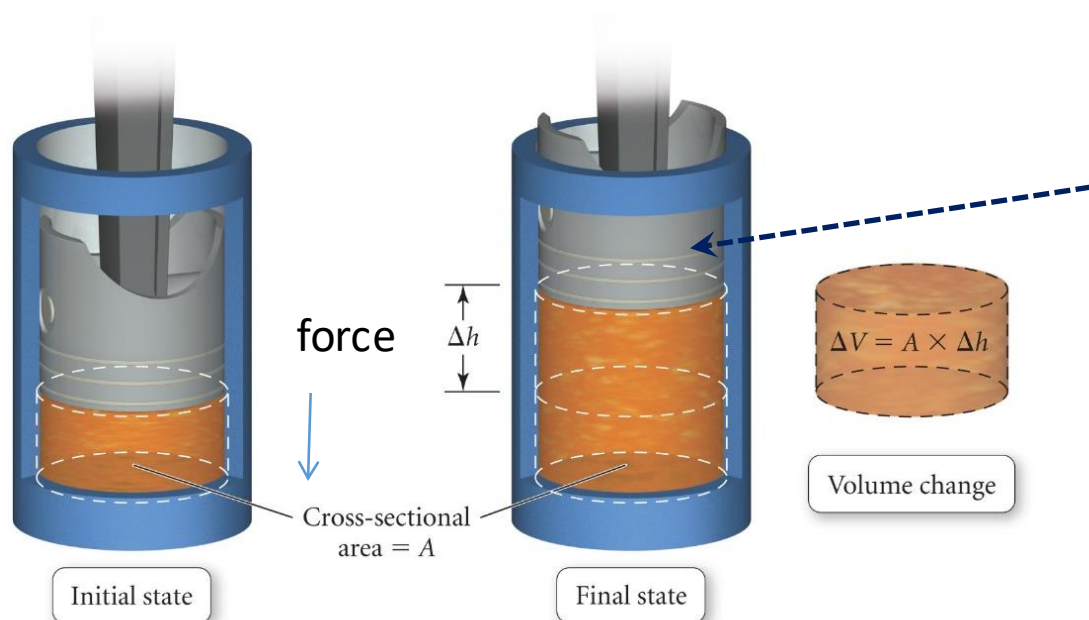| Learning Objective	Openstax 2e Chapter
Work	**5.3**
The First Law of Thermodynamics	**5.3**
State Functions	**5.3**

When volume is not constant: Pressure-Volume (PV) Work

PV work is work that is the result of a volume change against an external pressure

- When gases expand, ΔV is positive, but the system is doing work on the surroundings, so w is negative.

- If the *external pressure is kept constant:*

 **Work = − External Pressure x Change in Volume**

  $$w = -P_{ex}\Delta V$$

A piston provides a closed system that can change its volume with constant P

force

Δh

$\Delta V = A \times \Delta h$

Volume change

Cross-sectional area = A

Initial state

Final state

Recall this reaction

2 KClO$_3$ (s) $\longrightarrow$ 2 KCl(s) + 3 O$_2$ (g)

Gas formed pushes against the atmosphere, so the volume increases, work is done on the surroundings

P_{atm}

P_{atm}

$P = 0$

heating

O_2

KClO$_3$

KCl
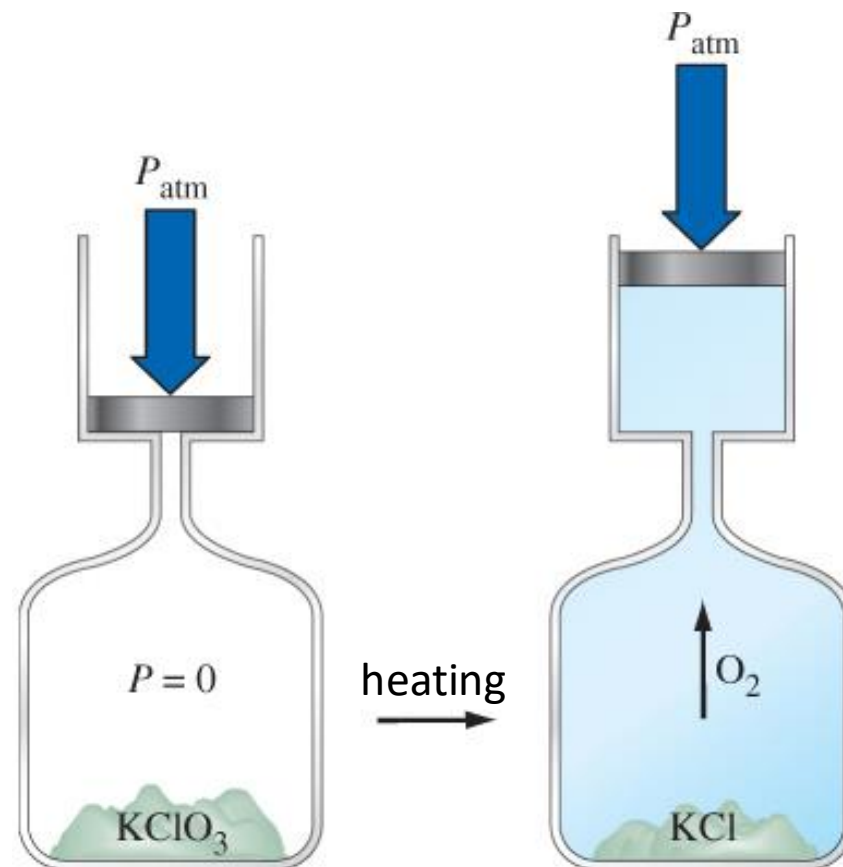
Example 1: In each of the following processes, determine whether any work is done *by* the system or *on* the system when the reaction is carried out at constant pressure in a vessel open to the atmosphere?

a) Decomposition of calcium carbonate to calcium oxide and carbon dioxide gas

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$.
Formation of a gas Δn_{gas}= +1 mol, results in an expansion, work is <u>by the system</u> done on the surroundings (w < 0)

b) Conversion of gaseous nitrogen dioxide to gaseous dinitrogen tetroxide
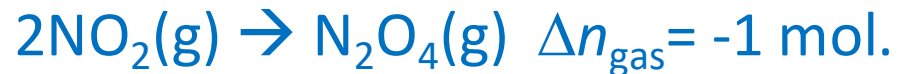
$2NO_2(g) \rightarrow N_2O_4(g)$ Δn_{gas}= -1 mol.
Work is done <u>on the system</u> by the surroundings (w > 0)

c) The neutralization of a 0.100 M NaOH solution by a 0.100 M HCl solution

No pressure volume work is done (i.e. no gases are formed or consumed, volume is constant to 3 sig figures or more)

The unit of w is Joules (J)

By SI units, 1 J = 1 Pa $\cdot$ m^3 = 1 N $\cdot$ m

Since 1 kPa = Pa/1000 and 1 L = 1000 x m^3,
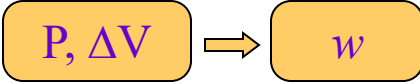
$\qquad$ 1 J = 1 kPa$\cdot$L

Sometimes, you may have atm x L as the result of PV work:

$$1\ atm\ \times\ L = 101325\ \text{Pa}\ \times\ 10^{-3}\ m^3 = 101.325\ \text{J}$$

(See slides in Module 3)

Example 2: If a balloon is inflated from 0.10 L to 1.85 L against an external pressure of 101.3 kPa, how much volume expansion work (in J) is done (ignoring the elastic work done on the balloon rubber)?

Given:	$V_{initial}$ = 0.10 L V_{final} = 1.85 L P_{ex} = 101.3 kPa
Find:	w
Concept Plan:	P, ΔV $\Rightarrow$ w
Relationships:	$w = -P_{ex} \Delta V$
Solution:	P_{ex} = 101.3 kPa ΔV = (1.85-0.10) L = 1.75 L $w = -P_{ex} \Delta V$ = - 101.3 kPa × 1.75 L = -177 kPa L = -177 J
Check:	The unit and sign are correct

Applying pressure with weighted pistons instead of the surrounding atmosphere

The force exerted (on the piston) by M is $\boxed{M \times g}$

Work due to gas expansion (lifting M) is
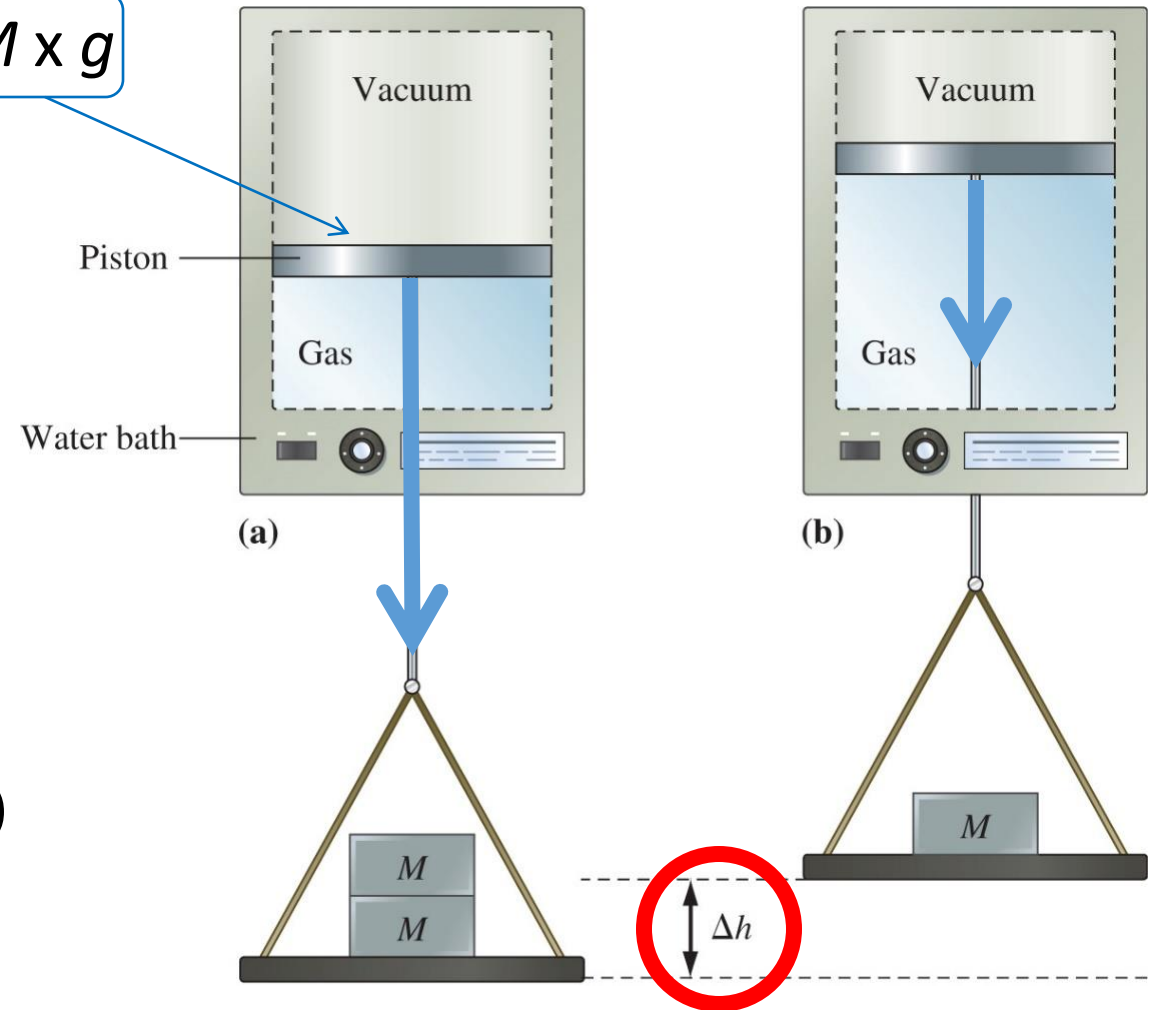$$w = -M \times g \times \textcolor{red}{\Delta h}$$

The piston moves by: $\Delta h = \Delta V / A$
(where A is the area of the piston)

Thus, $\qquad w = -M \times g \times \dfrac{\textcolor{red}{\Delta V}}{\textcolor{red}{A}}$

Recall: $P = force/area = (M \times g /A)$

Therefore: $\qquad \textcolor{red}{w = -P_{ext}\Delta V}$
(This is the usual expression for PV work!)

(a)

(b)

Vacuum

Vacuum

Piston

Gas

Gas

Water bath

M

M

M

Δh

M is suddenly removed

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Example 3: Suppose a piston-closed cylinder contains 0.100 mol He at 298 K and initially has two weights corresponding to an external pressure of 2.40 atm (see diagram left). One weight is quickly removed, and the remaining single weight (see diagram right) corresponds to an external pressure of 1.20 atm. How much work, in joules, is associated with the gas expansion at constant temperature when the weight is removed?

Analyze

We are given enough data to calculate the initial and final gas volumes (note that the identity of the gas does not enter into the calculations because we are assuming ideal gas behavior). With these volumes, we can obtain ΔV. The external pressure in the pressure–volume work is the *final* pressure: 1.20 atm. The product $-P_{ext} \times \Delta V$ must be multiplied by a factor to convert work in liter-atmospheres to work in joules.

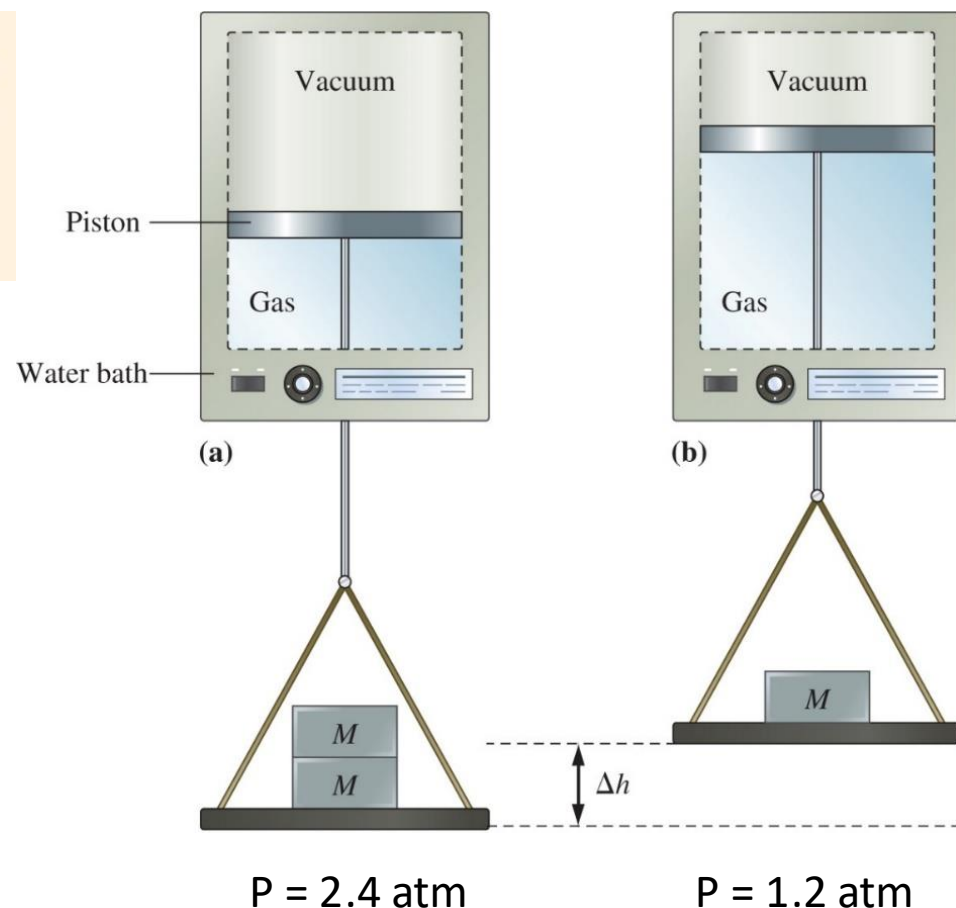### Solve

First calculate the initial and final volumes.

$$V_{initial} = \frac{nRT}{P_i} = \frac{(0.100\ mol)(0.0821\ atm\ L\ mol^{-1}\ K^{-1})(298\ K)}{2.40\ atm} = 1.02\ L$$

$$V_{final} = \frac{nRT}{P_f} = \frac{(0.100\ mol)(0.0821\ atm\ L\ mol^{-1}\ K^{-1})(298\ K)}{1.20\ atm} = 2.04\ L$$

$$P_{ext} = 1.20\ atm \times 101.325\frac{kPa}{atm} = 121.6\ kPa$$

$$\Delta V = 2.04\ L - 1.02\ L = 1.02\ L$$

$$w = -P_{ext}\Delta V = -121.6\ kPa \times 1.02\ L = -\mathbf{124\ J}$$

Vacuum

Vacuum

Piston

Gas

Gas

Water bath

(a)

(b)

M

M

M

Δh

P = 2.4 atm

P = 1.2 atm

First Law of Thermodynamics

Energy is not created nor destroyed during chemical or physical processes

The amount of heat (q) gained or lost by the system and the work (w) done on or by the system are used to change the internal energy of a system (ΔU).

$$\Delta U = q + w$$

Internal energy change

Heat gained or lost by system

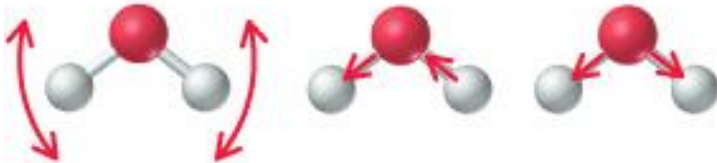Work done on the System or the surroundings

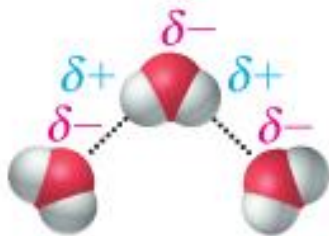|			
$q > 0$	system **gains** heat	$q < 0$	system **releases** heat energy
$w > 0$	system **gains** energy from work or work done on system	$w < 0$	system **releases** energy by doing work (on the surroundings)
$\Delta U > 0$	system **gains** energy	$\Delta U < 0$	system **releases** or loses energy

Translational

Rotational

Vibrational

Electrostatic
(Intermolecular attractions)

The **internal energy (*U*)** is the total amount of kinetic and potential energy a system possesses.

Some contributions to the internal energy of a system

- Translational kinetic energy.
- Molecular rotation.
- Bond vibration.
- Intermolecular attractions.
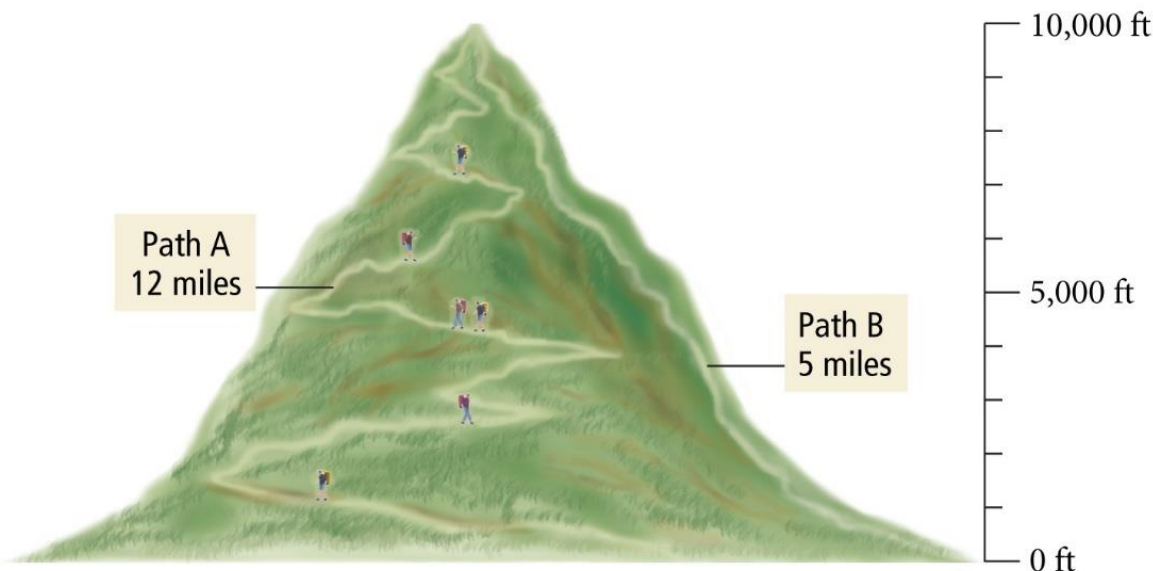- Chemical bonds.
- Electron motions.
- Nuclear energy.

Internal Energy (U) is a State Function

The change in the internal energy (U) of a system only depends on the amount of energy in the system at the beginning and end
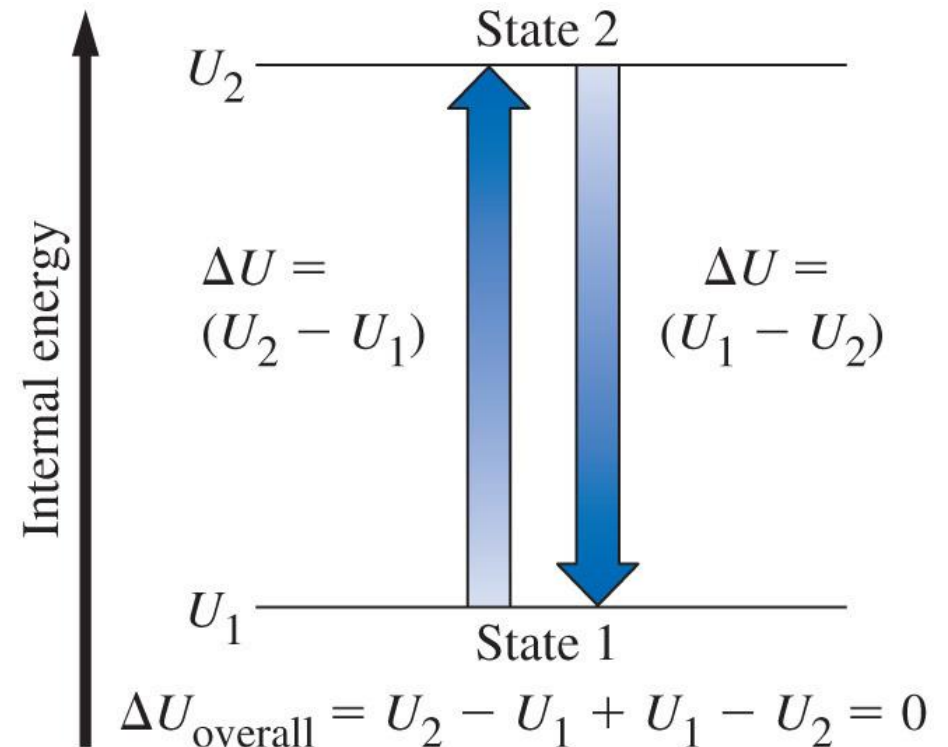
- **A state function** is a mathematical function whose result only depends on the initial and final conditions, not on the process used
- Otherwise stated, the value of a state function depends on the state of the system, and not on how the state is established
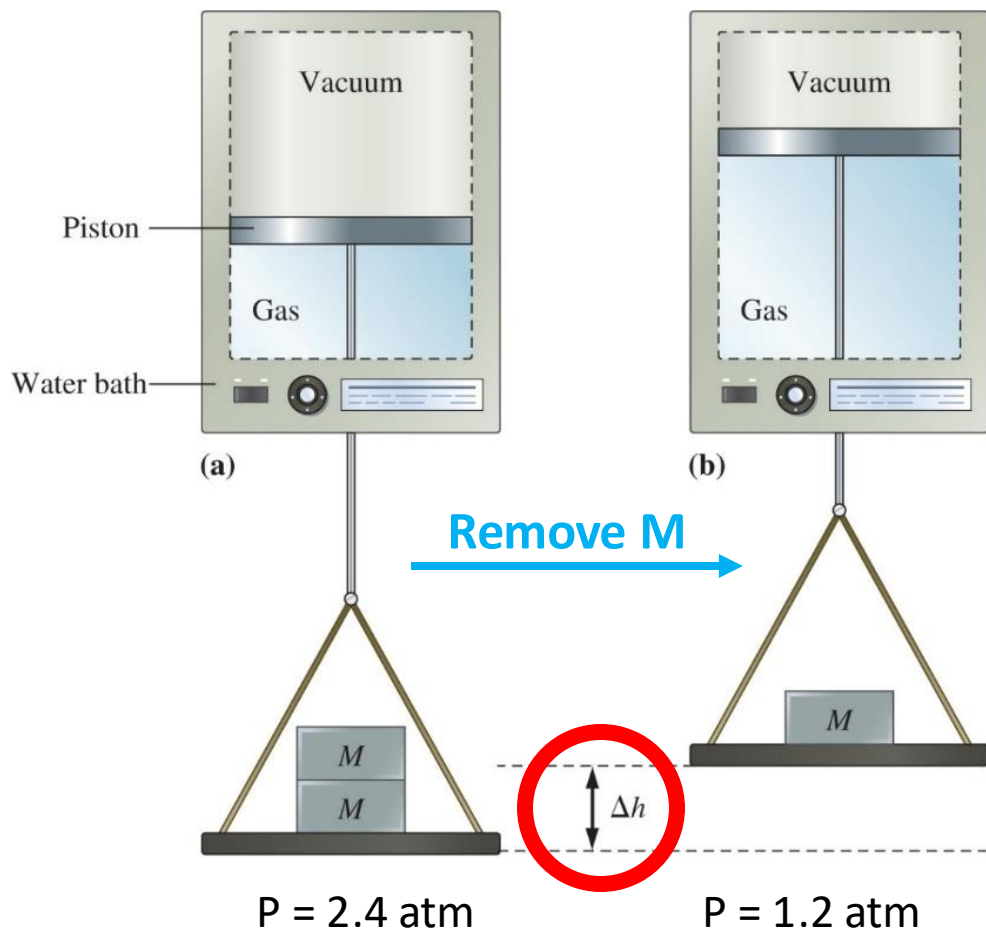
A State Function

Change in altitude depends only on the difference between the initial and final values, not on the path taken.

Path A
12 miles

Path B
5 miles

10,000 ft

5,000 ft

0 ft

U_2 — State 2

U_1 — State 1

$\Delta U = (U_2 - U_1)$

$\Delta U = (U_1 - U_2)$

Internal energy

$\Delta U_{overall} = U_2 - U_1 + U_1 - U_2 = 0$

But q and w are NOT state functions!

(a) Vacuum / Piston / Gas / Water bath / M / M / P = 2.4 atm
Remove M
(b) Vacuum / Gas / M / Δh / P = 1.2 atm

Vacuum / Piston / Gas / Water bath / State 1 / Δh/2 / P = 2.4 atm
Remove M/2
Vacuum / Gas / Intermediate state / Δh/2 / Δh / P = 1.8 atm
Remove M/2
Vacuum / Gas / State 2 / Δh / P = 1.2 atm

P = 2.4 atm Step 1 → P = 1.8 atm Step 2 → P = 1.2 atm
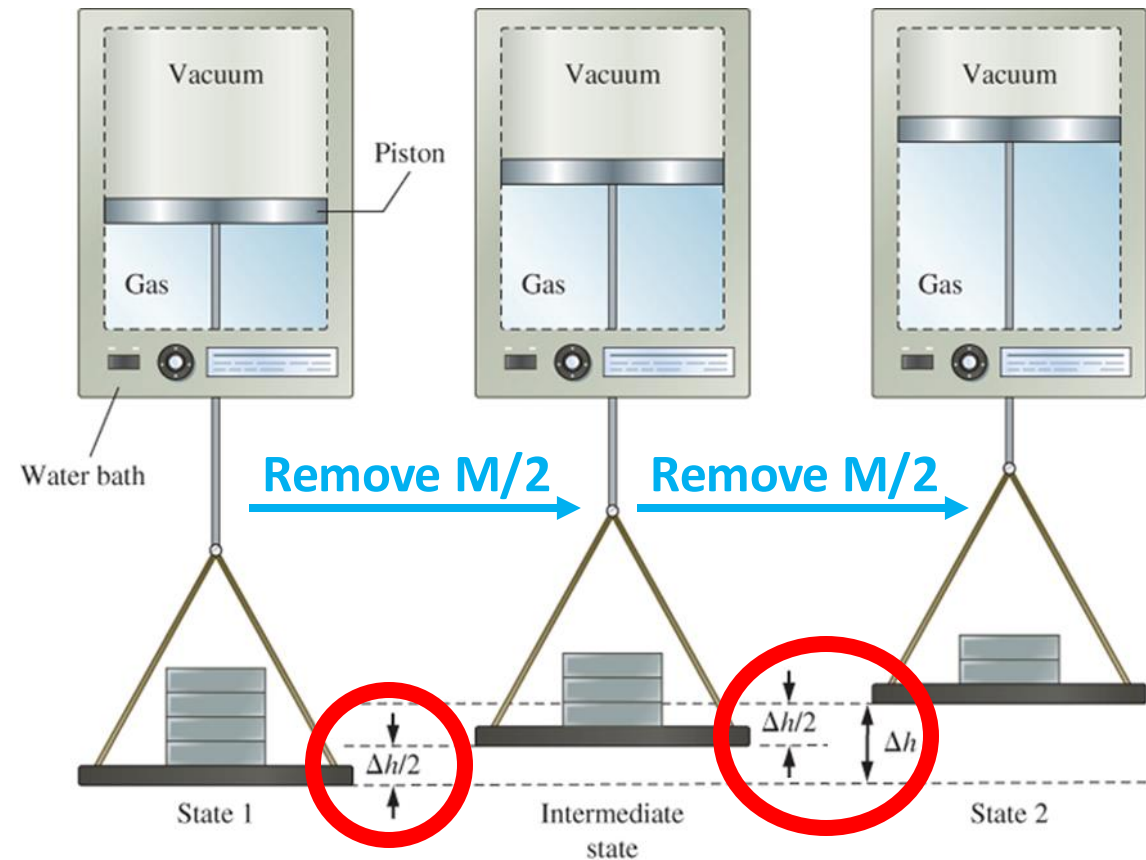
Example 3 (Slide 7): **One step isothermal expansion**

ΔV = 1.02 L, against P_{ext} = 1.20 atm

$w = -P_{ext} \cdot \Delta V$ = - 1.20 atm x 101.3 kPa/atm x 1.02 L

w = −124 J

How much work is done in this two-step expansion?

Initial P_{ext} = 2.40 atm, Step 1 expands against 1.80 atm, and Step 2 against 1.20 atm.

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Lets Examine Two-Step Expansion

Remove M/2

Remove M/2

Vacuum
Piston
Gas
Water bath

Vacuum
Gas

Vacuum
Gas

$\Delta h/2$

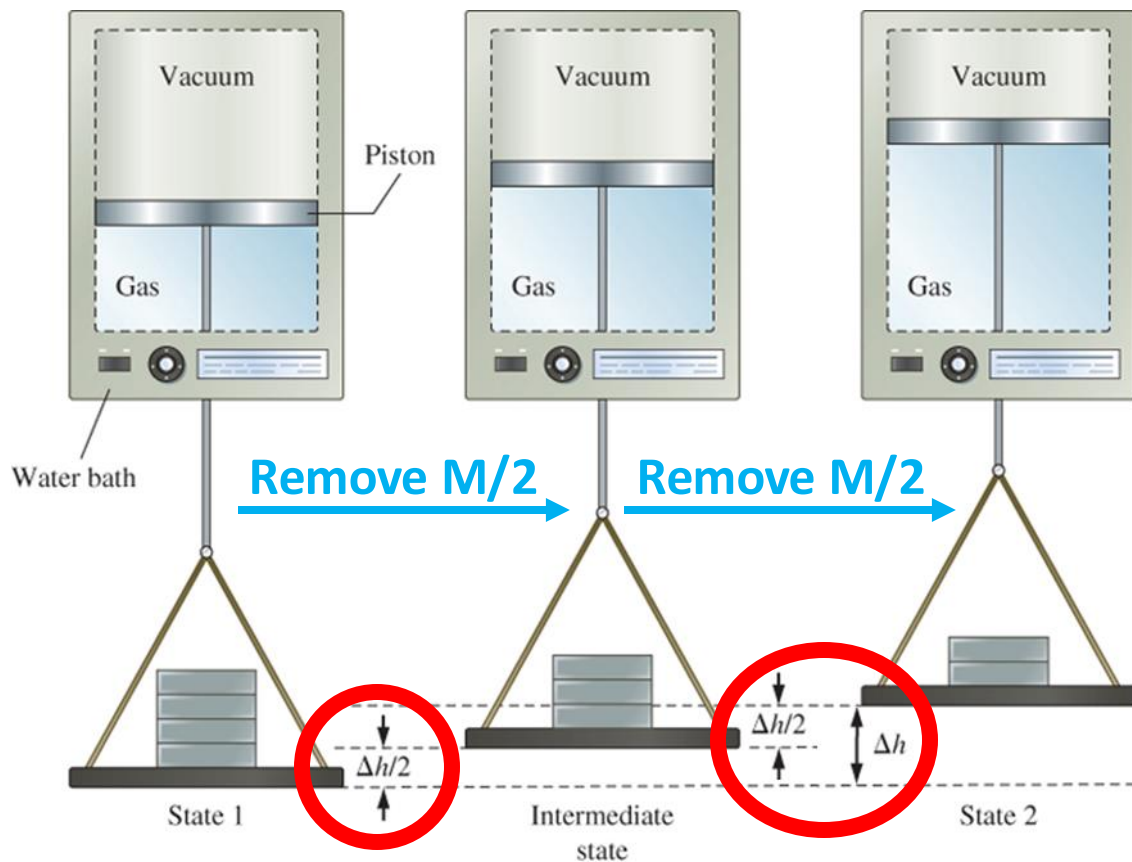$\Delta h/2$ Δh

State 1   Intermediate state   State 2

$P_0 = 2.4$ atm $\xrightarrow{\text{Step 1}}$ $P_1 = 1.8$ atm $\xrightarrow{\text{Step 2}}$ $P_2 = 1.2$ atm

How much work is done in this two-step expansion?

Known: $P_0 = 2.40$ atm $V_0 = 1.02$ L
$P_{ext1} = P_1 = 1.80$ atm
$P_{ext2} = P_2 = 1.20$ atm

Find: work in each step, w_1, w_2, and then $w_1 + w_2$

Step 1: $P_0 V_0 = P_1 V_1$ to find V_1
$V_1 = 2.40$ atm $\times$ 1.02 L / 1.80 atm = 1.36 L
$w_1 = - P_{ext1} \times (V_1 - V_0)$
$w_1 = - 1.80$ atm $\times$ 101.3 kPa/atm $\times$ 0.34 L
$w_1 = - 62$ J (*note only 2 sig figs*)

Step 2: $P_1 V_1 = P_2 V_2$ to find V_2
$V_2 = 2.04$ L
$w_2 = - P_{ext2} \times (V_2 - V_1)$
$w_2 = -1.20$ atm $\times$ 101.3 kPa/atm $\times$ 0.68 L
$w_2 = - 82.7$ J = 83 J

Total work: $w = w_1 + w_2 = (-62) + (-83) = $ **- 145 J**
Conclusion: More work is done on the surroundings in the two-step expansion than the one-step process (-124 J).

Different q and w values leading to the same ΔU
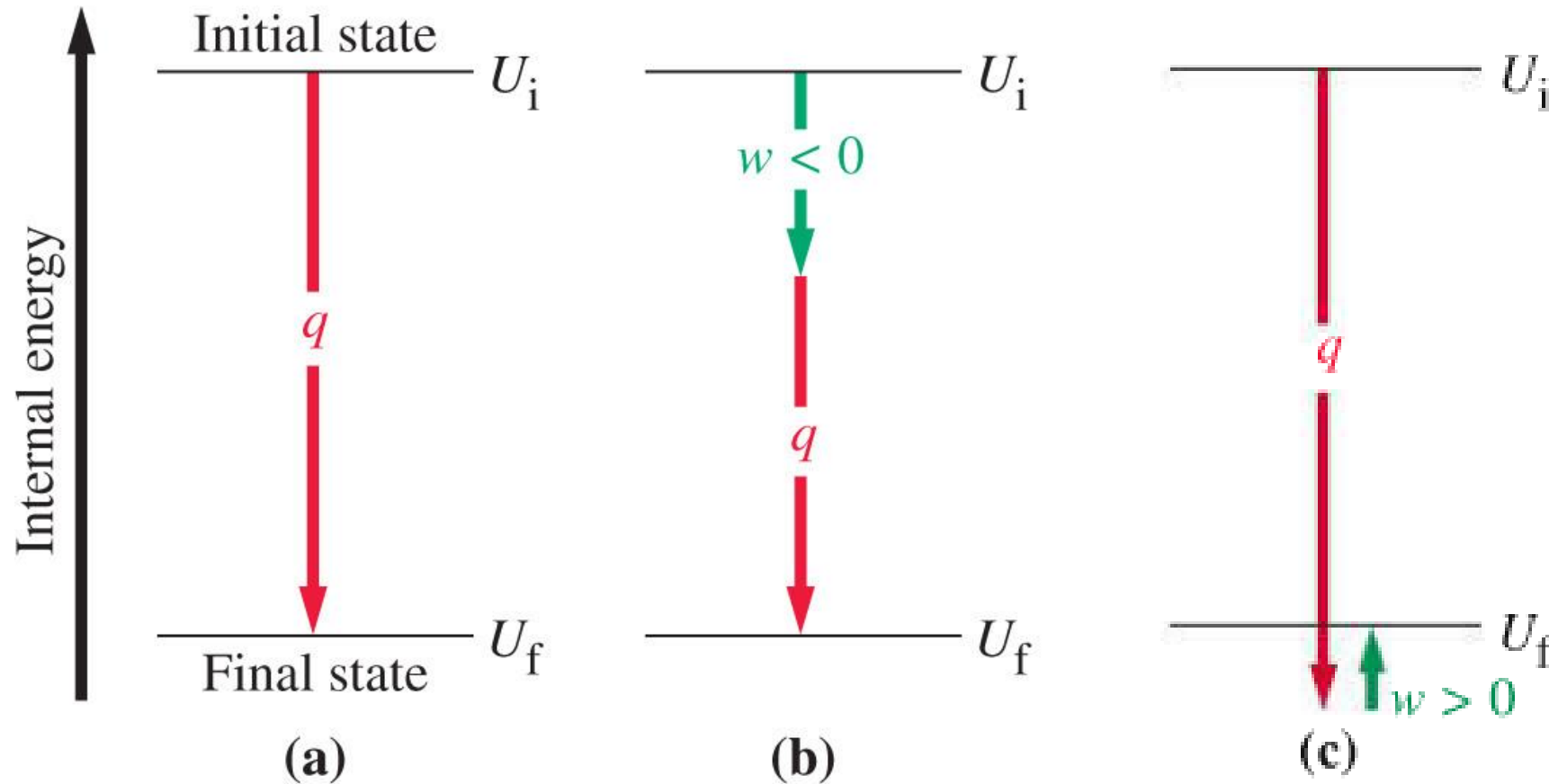
Three different paths leading to the same internal energy change (ΔU) in a system. Note that the values of q and w are different in all three processes.