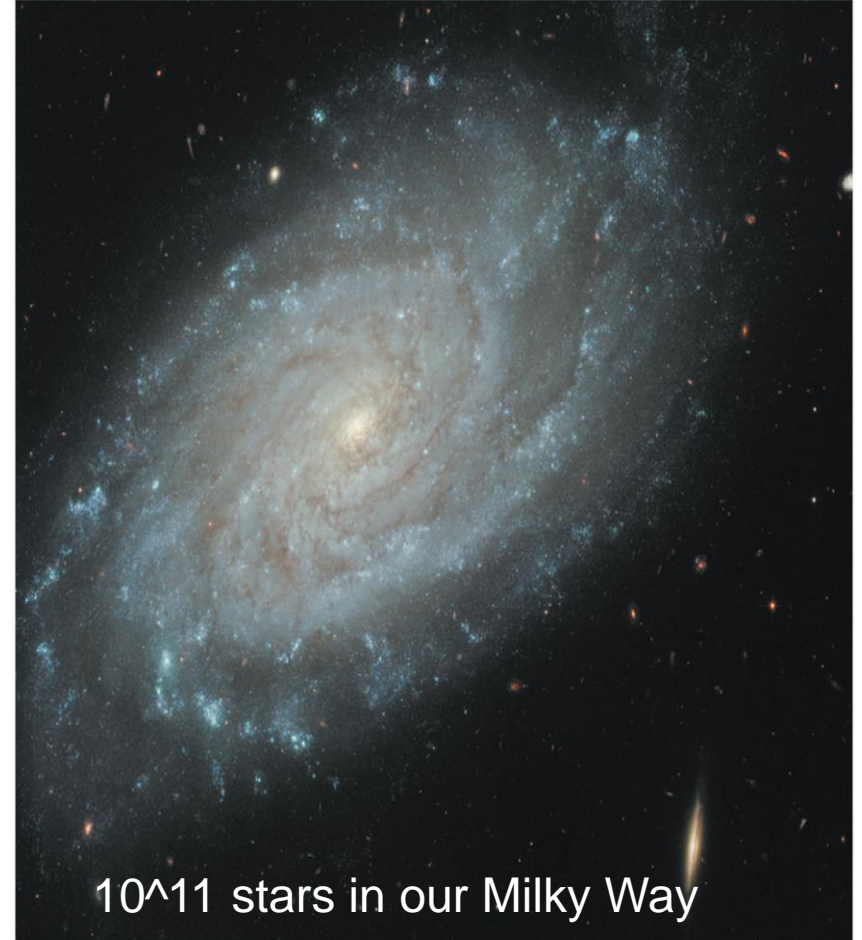


Chapter 15: Thermal Properties of Matter



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Chapter 15 Thermal Properties of Matter

- To understand the mole and Avogadro's number.
- To understand equations of state.
- To study the kinetic theory of ideal gas.
- To understand heat capacity.
- To learn and apply the first law of thermodynamics.
- To study thermodynamic processes.
- To understand the properties of an ideal gas.

Goals

- Relate the macroscopic properties to the microscopic properties
- Gain an understanding of the thermal properties of matter
- Consider various phases of matter: gas, liquid, and solid and conditions under which they occur

15.1 The Mole and Avogadro's Number

- Because atoms and molecules are so small, any practically meaningful amount of a substance contains a huge number of atoms or molecules. Therefore, it is more convenient to use a rather huge **measuring unit** to “count” their numbers.
- The **Avogadro's number**, $N_A = 6.022 \times 10^{23}$ molecules/mole, is such a measuring unit.
- 1 **mole** of a pure chemical element or compound contains $N_A = 6.022 \times 10^{23}$ identical atoms or molecules.
- The **molar mass** (M) is the mass of 1 mole of a pure chemical element or compound. It is equal to the Avogadro's number multiplying the mass of an atom or molecule (m).

$$M = N_A m$$

- The **total mass** of a system containing n moles of a substance:

$$m_{total} = nM$$

- The **total number** of particles in n moles of a substance:

$$N_{total} = nN_A$$

Example:

Carbon-12 ($^{12}_6\text{C}$)

$$m = 1.99 \times 10^{-23} \text{ g}$$

(a) The molar mass

$$M = N_A m = 12.0 \text{ g}$$

(b) The total mass of 1.5 moles of $^{12}_6\text{C}$

$$m_{total} = nM = 18.0 \text{ g}$$

(c) Number of atoms in 1.5 moles of $^{12}_6\text{C}$

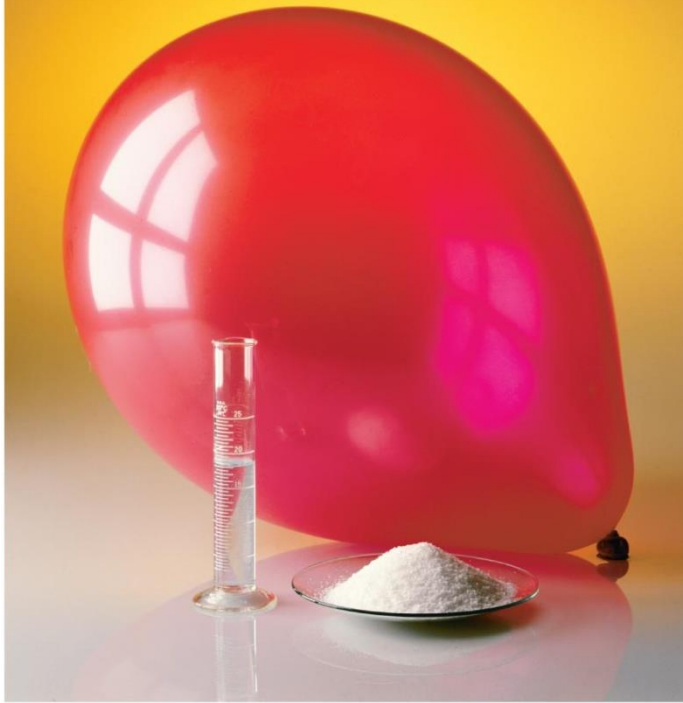
$$\begin{aligned} N_{total} &= nN_A \\ &= 9.03 \times 10^{23} \end{aligned}$$

Avogadro's Number

- A number to describe a set count of atoms, like "dozen" is a standard set for eggs.
- Because atoms are so small, it must be a huge number: 6.022×10^{23} .
- To put that number in perspective, count all the stars. That number would be approximately 100 billion (1.0×10^{11}).
- It would take a trillion (1.0×10^{12}) Milky Way galaxies to contain as many stars as there are particles in a mole. Again, because atoms are tiny.



1 mole each of several familiar substances



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Macroscopic parameters: pressure, volume, temperature, and mass.

Microscopic parameters: speeds, kinetic energies, momentum and masses of individual molecules.

Ideal gas can relate the macroscopic and microscopic parameters.

Phases of matters: gas, liquid, and solid.

Use the mole as the unit to describe the quantity of material (rather than mass).

1 mole (1 mol) is the amount of a substance that contains as many molecules or atoms as there are inside 0.012kg of carbon 12

Avogadro's number $N_A = 6.022 \times 10^{23}$ molecules/mole. Molar mass M of a substance is the mass of 1mol.

$$M = N_A \cdot \underbrace{m}_{\text{mass of a single molecule}}$$

$$m_{\text{Total}} = n \cdot M \quad (\text{Total mass} = \text{number of mol} \times \text{molar mass})$$

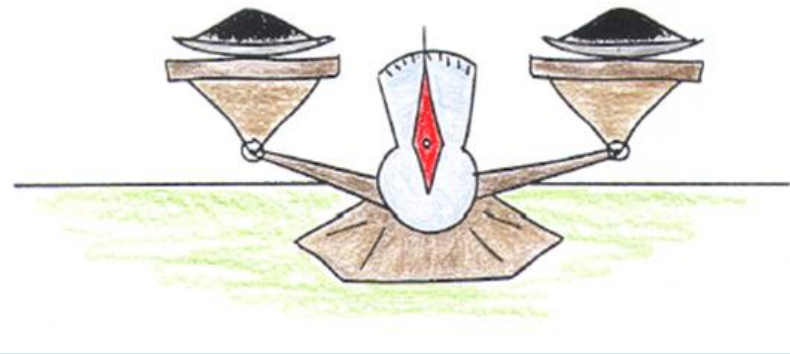
$$\begin{aligned} \text{Mass of an H-atom: } m_H &= \frac{M_H}{N_A} = \frac{1.008 \frac{\text{g}}{\text{mol}}}{6 \times 10^{23} \frac{\text{atom}}{\text{mol}}} \\ &= 1.67 \times 10^{-24} \frac{\text{g}}{\text{atom}} \end{aligned}$$

$$\begin{aligned} \text{Mass of an } O_2\text{-atom: } m_{O_2} &= \frac{M_{O_2}}{N_A} = \frac{(16 \cdot 2) \frac{\text{g}}{\text{mol}}}{6 \times 10^{23} \frac{\text{atom}}{\text{mol}}} \\ &= 53 \times 10^{-24} \frac{\text{g}}{\text{atom}} \end{aligned}$$

Ticker - Questions 1

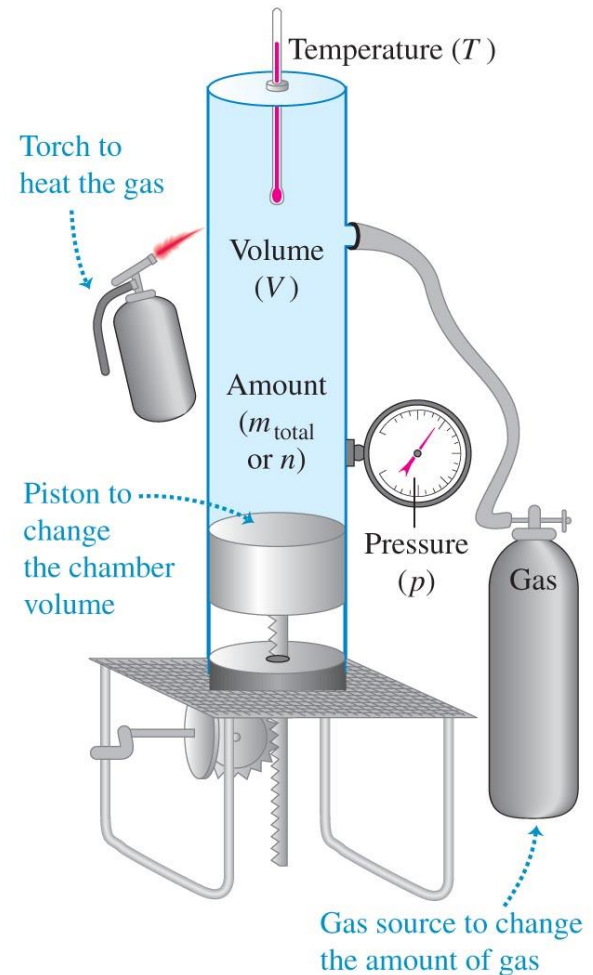
Which has more atoms: a one gram sample of carbon-12, or a one gram sample of carbon-13?

- a) carbon-12
- b) carbon-13



15.2 Equation of State

- Imagine that we can work on the device on the right.
- We may take different actions and expect some results: If we heat it up, temperature (T) rises and the volume (V) expands; if we compress it, pressure (p) increases; if we add more gas (n) into the system, pressure (p) increases and volume expands (V), etc.
- **Question:** how are these physical quantities (T , p , V , n , etc.) related to each other for a given system?
- The **equation of state:** a mathematical equation relates these physical quantities to each other. These physical quantities are also known as **state variables** or **state coordinates**.



Equations of state with state variables

Ideal gas equation:

$$pV = nRT \quad [J = \frac{N}{m^2} m^3 = mol \frac{J}{mol * K} K]$$

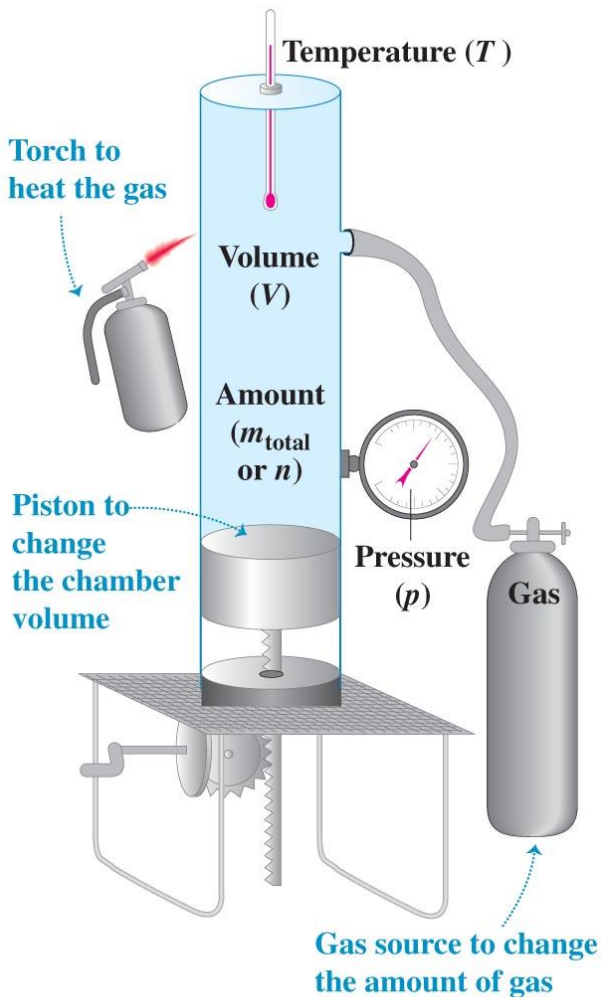
$$R = 8.3145 \frac{J}{mol * K} = 0.08206 L * \frac{atm}{mol * K}$$

$$pV = \frac{m_{total}}{M} RT \rightarrow \rho = \frac{m_{total}}{V} = \frac{pM}{RT}$$

Remember $m_{total} = n \cdot M$ and $M = \text{molar mass}$

For a constant mass (number of moles) of an ideal gas

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} = nR = \text{constant}$$



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STP (standard temperature and pressure):

$$0^\circ C = 273K \text{ and } 1 \text{ atm} = 1.013 \times 10^5 Pa$$

How large is a container to keep 1mole of gas at STP?

$$V = \frac{nRT}{p} = \frac{1 \text{ mol} * 8.314 \frac{J}{\text{mol} * K} * 273K}{1.013 \times 10^5 Pa} = 0.0224 m^3 * \frac{1000L}{1m^3} = 22.4 L$$

The Ideal-Gas Equation or Ideal-Gas Law

- For most gases, their state variables very closely obey a simple relationship:

$$pV = nRT.$$

- $R = 8.3145 \text{ J}/(\text{mol}\cdot\text{K})$ is the ideal-gas constant and is a universal constant for all gasses.

- T is measured in Kelvin (K).

- The above relationship is known as the **ideal-gas equation**, or, the **ideal-gas law**.

- We may re-write the ideal-gas equation, replacing n by m_{total}/M ,

$$pV = \frac{m_{\text{total}}}{M} RT$$

- We may write the ideal-gas equation in terms of the density of the gas, $\rho = m_{\text{total}}/V$,

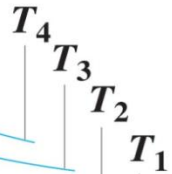
$$\rho = \frac{pM}{RT}$$

PV-diagrams

Each curve represents pressure as a function of volume for an **ideal gas** at a single temperature.

For each curve, pV is constant and is directly proportional to T (Boyle's law).

$$T_4 > T_3 > T_2 > T_1$$



Isotherm = (same temperature) curve representing pV -behavior at a specific temperature

Critical temperature = temperature above which material does not separate into two phases. It goes smoothly without a phase transition.

Not ideal gas

$$T_4 > T_3 > T_c > T_2 > T_1$$

Above the critical temperature T_c there is no liquid-vapor phase transition.

Below T_c , the material condenses to liquid as it is compressed.

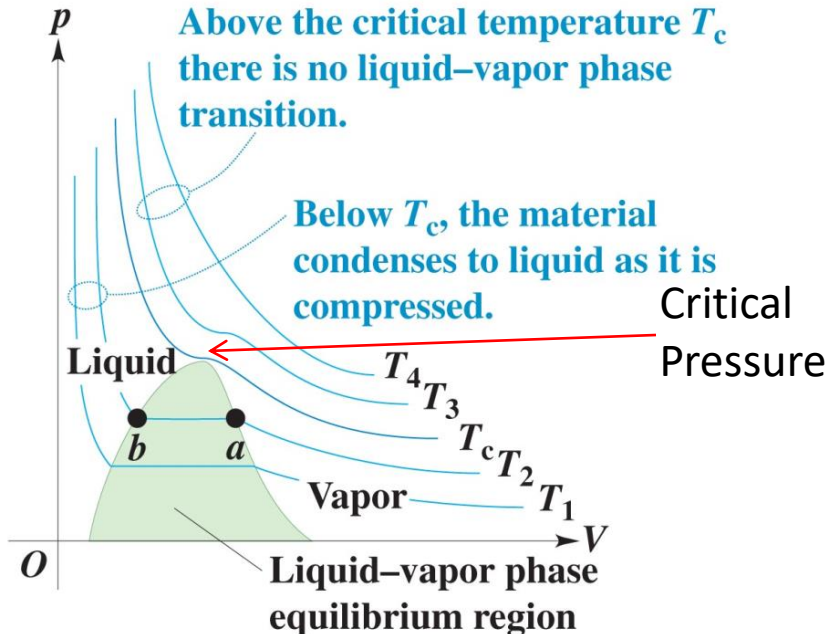
Critical Pressure

Liquid

Vapor

Liquid-vapor phase equilibrium region

The area under a pV -curve represents the work done by the system during a change in volume equivalent to heat transfer and the change of the internal energy.

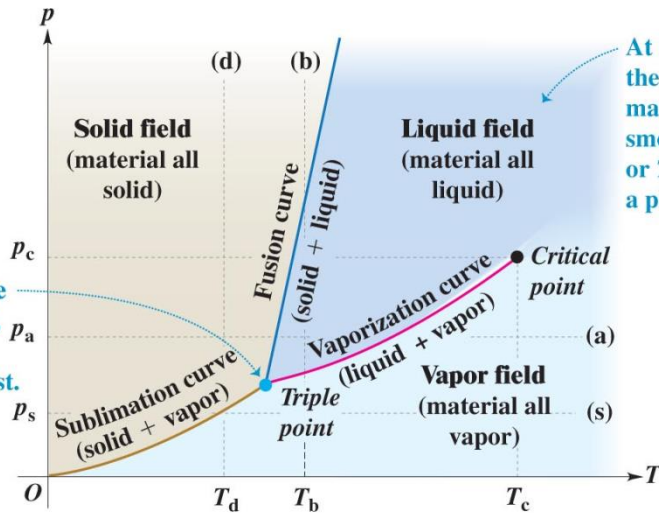


PT-phase diagram

A graph which indicates what phase occurs at a particular p and V

At T and p values above the critical point, the material properties change smoothly with changing p or T, rather than undergoing a phase change.

At the triple point, solid, liquid, and vapor coexist.



(Line a) → horizontal = constant pressure reducing T yields: vapor, liquid, and solid phases

(Line b) → vertical = constant temperature increasing p yields: vapor, liquid, and solid phases

(Line s) → horizontal = constant pressure sublimation or direct transfer of solid to liquid (no vapor phase).
Example: dry ice ↔ carbon dioxide

Triple point = all three phases coexist at a unique pressure-temperature combination.

Critical point = distinction between liquid and gas disappears (properties change gradually)

TABLE 15.1 Triple-point data

Substance	Temperature, K	Pressure, Pa
Hydrogen	13.8	0.0704×10^5
Neon	24.57	0.432×10^5
Nitrogen	63.18	0.125×10^5
Oxygen	54.36	0.00152×10^5
Ammonia	195.40	0.0607×10^5
Carbon dioxide	216.55	5.17×10^5
Water	273.16	0.00610×10^5

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TABLE 15.2 Critical-point data

Substance	Critical temperature, K	Critical pressure, Pa
Helium ($\frac{4}{2}$ He)	5.3	2.29×10^5
Hydrogen	33.3	13.0×10^5
Nitrogen	126.2	33.9×10^5
Oxygen	154.8	50.8×10^5
Ammonia	405.5	112.8×10^5
Carbon dioxide	304.2	73.9×10^5
Water	647.4	221.2×10^5

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15.3 Kinetic Theory of an Idea Gas

- The **question**: how are measurable macroscopic variables related to microscopic properties of the atoms and molecules?
- The **idea gas**: We will treat atoms or molecules as point particles undergoing rapid elastic collisions with each other and the walls of the container in the given volume. The **potential energies** due to all the forces **are ignored**.
- The **process** is to apply Newton's laws to establish the relationship between microscopic and macroscopic quantities.
- The **goals** are to understand:
 - the pressure of an ideal gas;
 - the ideal-gas equation;
 - the temperature of an ideal gas;
 - internal energy of an ideal gas;
 - the heat capacity of an ideal gas;
 - etc.

Kinetic Molecular Theory of an Ideal Gas

Pressure (the impulse of molecule collision with container wall)

(a) momentum change in one collision event: $2m|v_x|$

(b) total momentum change in time interval Δt :

$$\Delta P_x = \left(\frac{1}{2}\right) \left(\frac{N}{V}\right) (A|v_x|\Delta t)(2m|v_x|) = \frac{NAmv_x^2\Delta t}{V}$$

(c) Force on the wall is: $F_x = \frac{\Delta P_x}{\Delta t} = \frac{NAmv_x^2}{V}$

(d) Pressure on the wall is: $p = \frac{F_x}{A} = \frac{Nm v_x^2}{V} \dots\dots(15.6)$

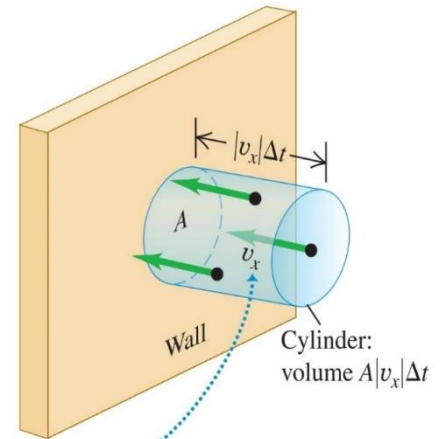
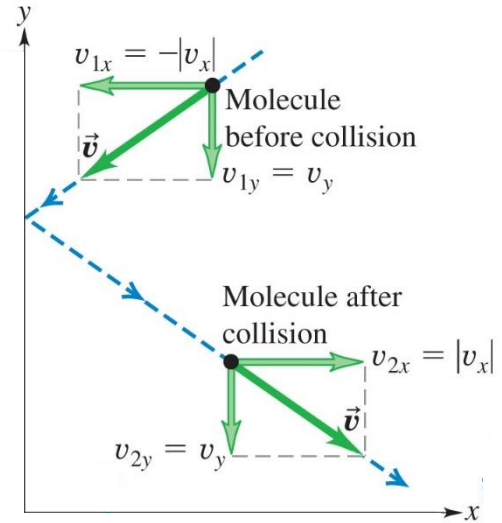
(e) Molecules with a distribution of velocities? Take average.

$$p = \frac{F_x}{A} = \frac{Nm(v_x^2)_{av}}{V} = \frac{N}{V} \left[\frac{1}{3} m(v^2)_{av} \right] = \frac{1}{V} \left[\frac{2}{3} K_{tr} \right],$$

where $K_{tr} = N \left[\frac{1}{2} m(v^2)_{av} \right]$ is the total kinetic energy.

(f) Compare with the ideal-gas equation: $pV = nRT$, we have the total kinetic energy of the gas molecules,

$$K_{tr} = \frac{3}{2} nRT \dots\dots\dots(15.7)$$



All molecules are assumed to have the same magnitude $|v_x|$ of x velocity.

The Boltzmann Constant

- The total kinetic energy of all the particles in an ideal gas is $K_{tr} = \frac{3}{2}nRT$.
- It relates the microscopic properties to measurable macroscopic quantities.
- The kinetic is independent of the mass of the atoms or molecules.
- The average kinetic energy per atom or molecule is

$$K_{av} = \frac{1}{2} m(v^2)_{av} = \frac{K_{tr}}{nN_A} = \frac{\frac{3}{2}nRT}{nN_A} = \frac{3}{2} \left(\frac{R}{N_A}\right)T.$$

- Define the **Boltzmann constant**

$$k = \frac{R}{N_A} = \frac{8.314 \text{ J}/(\text{mol}\cdot\text{K})}{6.022 \times 10^{23} / \text{mole}} = 1.381 \times 10^{-23} \text{ J/K},$$

then, $K_{av} = \frac{1}{2} m(v^2)_{av} = \frac{3}{2} kT \dots\dots\dots(15.8)$

which is independent of the details of the particles, such as the mass.

- We can re-write the ideal-gas equation to $pV = nRT = n(kN_A)T$,
or $pV = NkT \dots\dots\dots(15.9)$

Gas constant R = 8.3144598 J/ (mol K)

- 4 steps:
1. Find Δp /collision
 2. Find # of collisions
 3. Find force/area
 4. Find p and relate to ideal gas law

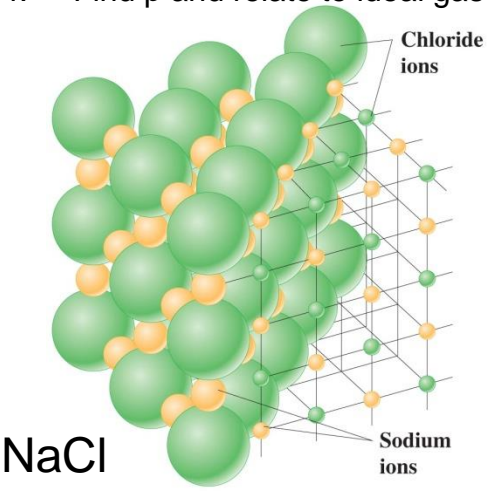
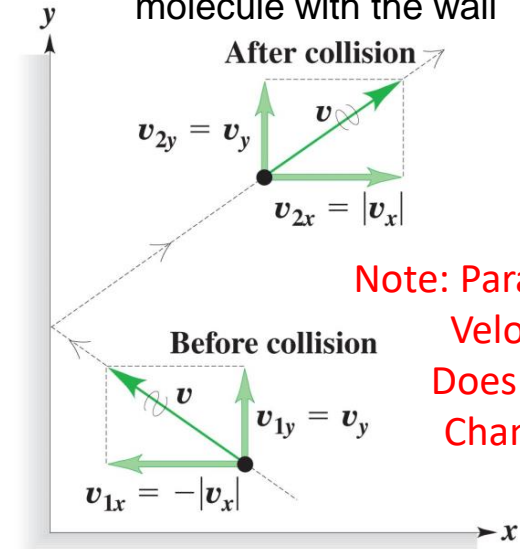
Molecular model of an ideal gas

Aim: derive pressure in the molecular picture

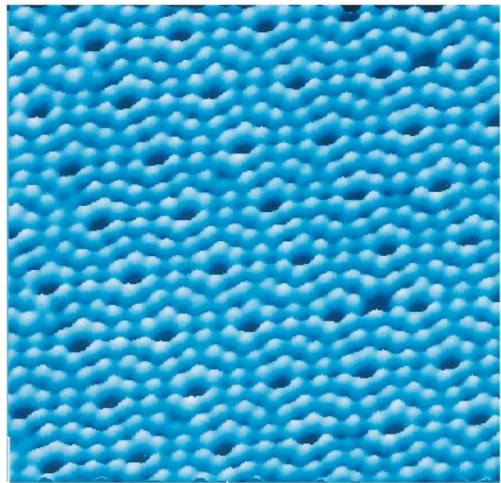
Atoms sizes $\approx 10^{-10}$ m
 Largest molecule sizes $\approx 10^{-6}$ m

In gas molecules are in motion.
 In solids molecules vibrate around centers.
 In liquids molecules vibrate with more freedom in movement.

Elastic collision of a molecule with the wall



NaCl
 silicon



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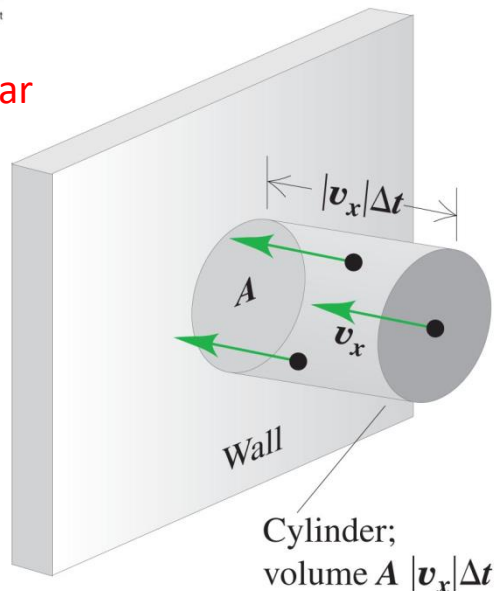
1. Total change of momentum Kinetic molecular theory of an ideal gas:

assume all molecules to have the same velocity
 $\Delta P = m|v_x| - (-mv_x) = 2mv_x$

2. The number of collisions with wall (area A) during Δt is

$$\# = \frac{1}{2} \frac{N}{V} (A|v_x|\Delta t)$$

$$\Delta P_x = \frac{1}{2} \frac{N}{V} (A|v_x|\Delta t)(2mv_x) = \frac{NAmv_x^2 \Delta t}{V}$$



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Small 'p' → pressure
 Large 'P' → momentum

3. $\frac{\Delta P_x}{\Delta t} = \frac{NAmv_x^2}{V} = F; \frac{dP}{dt} = ma = F$ Remember Newton's law

4 expression for pressure

Aim: The average translational kinetic energy of a molecule depends only on T, not p or V

$$p = \frac{F}{A} = \frac{Nmv_x^2}{V} \rightarrow pV = Nmv_x^2$$

Express v_x^2 in terms of the average in v^2 of all molecule

$$v_{av}^2 = v_{xav}^2 + v_{yav}^2 + v_{zav}^2 = 3v_{xav}^2 \text{ (no distinction between x, y, and z)} \rightarrow \bar{v}_x^2 = \frac{1}{3}\bar{v}^2$$

$$pV = \frac{1}{3} \underbrace{N}_{\text{number of molecules}} m \underbrace{\bar{v}^2}_{\text{average translational kinetic energy of a single molecule}} = N \frac{2}{3} \left(\frac{1}{2} m \bar{v}^2 \right) = \frac{2}{3} \underbrace{K_{tr}}_{\text{Total translational energy}}$$

$$\text{Compare; } pV = nRT = \frac{2}{3} K_{tr} \rightarrow K_{tr} = \frac{3}{2} nRT$$

Venus is just like in "Goldie Locks", too hot and Mars is too cold but Jupiter is just right.

Note: H_2 exceeds the escape speed. Hydrogen as the lightest gas has an average speed at a given temperature than other heavier gases.

Boltzmann Constant:

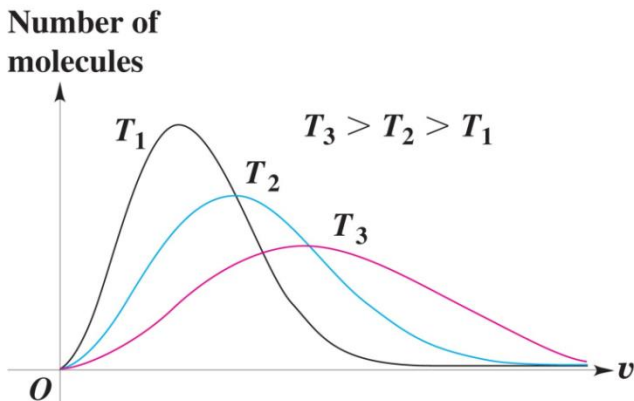
$$\text{Escape speed } v_{as} = \sqrt{\frac{2Gm_E}{R_E}}$$

$$\underbrace{K_1 + U_1}_{\text{surface of earth}} = \underbrace{K_2 + U_2}_{\text{infinity}}$$

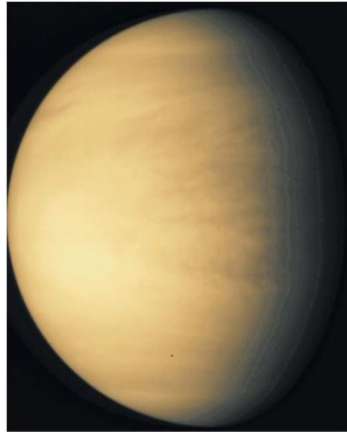
$$\frac{1}{2}mv^2 + \left(-G \frac{m_E m}{2E}\right) = 0 + 0$$

Earth and Jupiter to scale

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$$\bar{K}_{molecular} = \frac{K_{tr}}{N} = \frac{3}{2} \frac{nRT}{N} = \frac{3}{2} \frac{nRT}{2nN_A} = \frac{3}{2} kT \rightarrow k = \frac{R}{N_A} = 1.38 \times 10^{-23} \frac{J}{\text{molecule} \cdot K}$$

Glicker - Questions 2

You heat a sample of air to twice its original temperature in a constant volume container. The average translational kinetic energy of the molecules is;

- A. Half the original value.
- B. Unchanged.
- C. Twice the original value.
- D. Four time the original value.

Molecular Speeds in an Ideal Gas

The average kinetic energy per atom or molecule:

$$K_{av} = \frac{1}{2} m(v^2)_{av} = \frac{3}{2} kT,$$

from which we obtain the root-mean-square velocity

$$v_{rms} = \sqrt{(v^2)_{av}} = \sqrt{\frac{3kT}{m}},$$

where m is the mass of an atom or molecule.

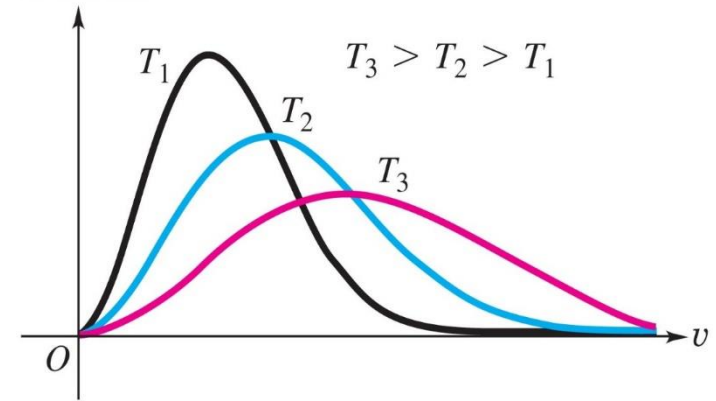
Since $kN_A = R$ and $mN_A = M$, we may re-write,

$$v_{rms} = \sqrt{\frac{3RT}{M}}.$$

Note: $(v^2)_{av} \neq (v_{av})^2 = 0$

Maxwell-Boltzmann Distribution of Molecular Speed

Number of
molecules



Example for Molecular speeds in an ideal gas

$$K_{av}(\text{molecule}) = \frac{1}{2}mv_{ev}^2 = \frac{3}{2}kT$$

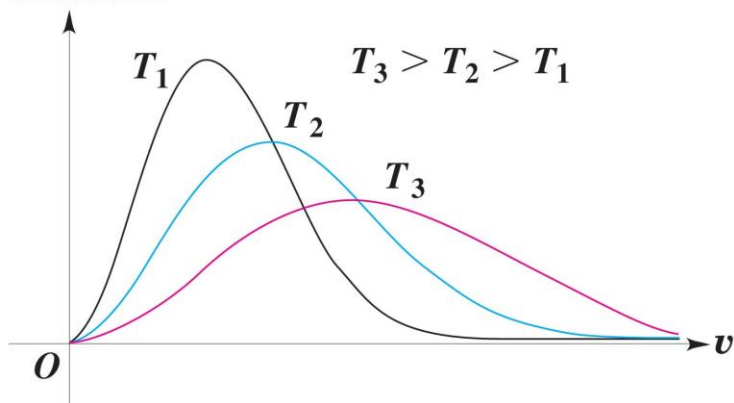
$$v_{rms} = \sqrt{v_{av}^2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

Consider O_2 as residual gas at 27°C . Find $\underbrace{K_{av}}_{\text{per molecule}}$ and $\underbrace{K_{tr}}_{\text{per mole}} \rightarrow 27^\circ\text{C}=300\text{K}$

$$K_{av} = \frac{1}{2}mv_{av}^2 = \frac{3}{2}kT = \frac{3}{2}(1.38 \times 10^{-23})(300\text{K}) = 6.21 \times 10^{-21}\text{J}$$

$$K_{tr} = \frac{3}{2}nRT = \frac{3}{2}(1\text{mol}) \underbrace{(8.3)}_{\left[\frac{\text{J}}{\text{mol.K}}\right]}(300\text{K}) = 3740\text{J}$$

Number of molecules



$$k = 1.38 \times 10^{-23} \left[\frac{\text{J}}{\text{mol.K}}\right]$$

Problem 15-68

(a) Find v_{rms} of the hydrogen atom for H in the sun ($T_{sun}=5800K$)

$$\frac{1}{2}mv_{rms}^2 = \frac{3}{2}kT \rightarrow v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3 * 1.38 \times 10^{-23} J * 5800 K}{1.67 \times 10^{-27} kg}} = 1.2 \times 10^4 \frac{m}{s} = 12 \frac{km}{s}$$

(b) What is the mass of an atom that has half the speed?

$$v_{rms}\sqrt{m} = \sqrt{3kT} = constant \rightarrow v_{rms,1}\sqrt{m_1} = v_{rms,2}\sqrt{m_2}$$
$$v_{rms,2} = \frac{1}{2}v_{rms,1}$$
$$m_2 = 4m_1 = 4 * 1.67 \times 10^{-27} = 6.68 \times 10^{-27} kg$$

Constant-Volume Molar Heat Capacity of an Ideal Gas

Consider an ideal gas with its **volume fixed**, when heat energy Q is added to or remove from the ideal gas, the total kinetic energy $K_{tr} = \frac{3}{2}nRT$ is changed by the same amount based on the conservation of energy (because, for an ideal gas, the potential energies due to all the forces are ignored):

$$Q = \Delta K_{tr} = \frac{3}{2}nR\Delta T = n\left(\frac{3}{2}R\right)\Delta T.$$

Therefore, the constant-volume molar heat capacity is

$$C_V = \frac{3}{2}R = 12.5 \text{ J}/(\text{mol}\cdot\text{K})$$

Note:

(a) The constant-volume molar heat capacity C_V given above is correct for monatomic gases and is independent of the details of the atoms, such as atomic masses.

(b) For gases of diatomic molecules, $C_V = \frac{5}{2}R = 20.8 \text{ J}/(\text{mol}\cdot\text{K})$

15.4 The Molar Heat Capacities

Note: In Chapter 14, we defined the **specific heat** as the heat energy required to raise the temperature of 1 kg of a substance by 1 °C (or 1 K).

Now, we are going to define a quantity called the **molar heat capacity**. Its meaning is similar to that of the specific heat, but it is defined in different units.

Question: How much heat energy Q is needed to raise n moles of a substance by a temperature ΔT ?

The **answer** is: $Q = nC\Delta T$

Note:

- (a) The heat energy is proportional to n and ΔT .
- (b) The proportionality constant C is called the **molar heat capacity**. It is the heat energy needed to raise the temperature of 1 mol of a substance by 1 °C (or 1 K).
- (c) C is in general material-dependent. Yet, it has some simple forms for an ideal gas.
- (d) The molar heat capacity has the units of J/(mol•K).
- (e) Q is defined positive if it is transferred into the system, and, negative otherwise.
- (f) Relationship with the specific heat c : $C = Mc$ (M is the molar mass)

Heat capacities

Specific heat capacity (previous chapter)

$$Q = m_{total}c\Delta T \rightarrow c = \text{specific heat capacity [J/kg}\cdot\text{K]} \quad (c(\text{water}) = \frac{1\text{cal}}{\text{g}\cdot\text{K}})$$

Molar heat capacity (novel fundamental level)

$$Q = nC\Delta T \rightarrow C \left[\frac{\text{J}}{\text{mol}\cdot\text{K}} \right] = \text{molar heat capacity}$$

Related to specific heat capacity c (small letter) by comparison with;

$$C = M\bar{c}$$

Molar mass M
Molar heat capacity C
Specific heat capacity \bar{c}

$$Q = m_{total}c\Delta T = \underbrace{M}_{\text{molar mass}} \underbrace{\tilde{n}}_{\text{number of moles}} c\Delta T$$

Change in translational kinetic energy

$$\left. \begin{aligned} \Delta K_{tr} &= \frac{3}{2}nR\Delta T \\ Q &= nC_V\Delta T \end{aligned} \right\} = nC_V\Delta T = \frac{3}{2}nR\Delta T$$

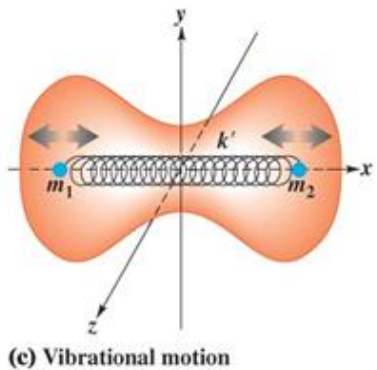
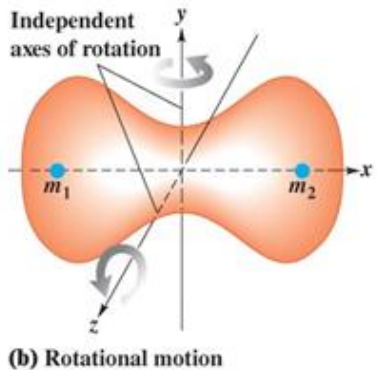
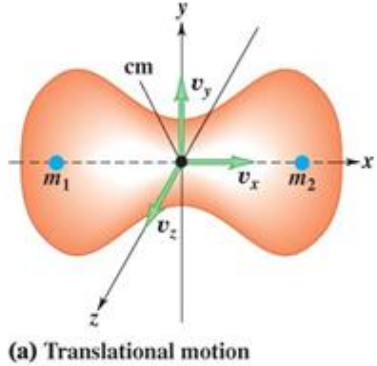
Energy gas (mono-atomic) $C_V = \frac{3}{2}R$

$$C_V = \frac{3}{2} \left[\underbrace{8.314}_{R} \frac{\text{J}}{\text{mol}\cdot\text{K}} \right] = 12.47 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

TABLE 15.3 Molar heat capacities of gases

Type of gas	Gas	C_V (J/(mol·K))
Monatomic	He	12.47
	Ar	12.47
Diatomic	H ₂	20.42
	N ₂	20.76
	O ₂	21.10
	CO	20.85
Polyatomic	CO ₂	28.46
	SO ₂	31.39
	H ₂ S	25.95

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Diatomic: $\rightarrow C_V = \frac{5}{2}R$

Poly-atomic: more degrees of freedom

A diatomic molecule can move in three ways: translation, rotation, and vibration. At lower temperature; only translation and rotation degrees are active and not vibration

15.6 Thermodynamics Processes

$$\Delta U = Q - W$$

- **Adiabatic:** no heat transfer in or out of the system

$$Q = 0$$

$$\Delta U = -W$$

- **Isochoric:** no volume change

$$V = \text{constant} \quad \text{or} \quad \Delta V = 0 \quad \text{or} \quad W = 0$$

$$\Delta U = Q$$

- **Isobaric:** no pressure change.

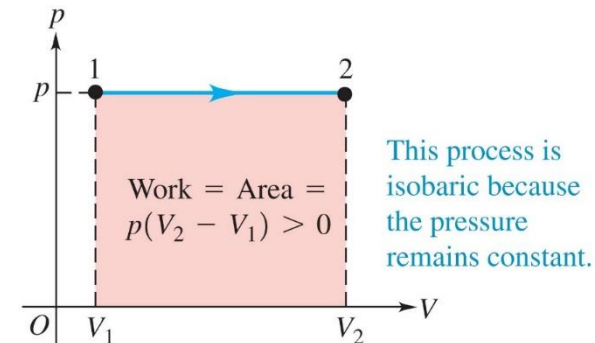
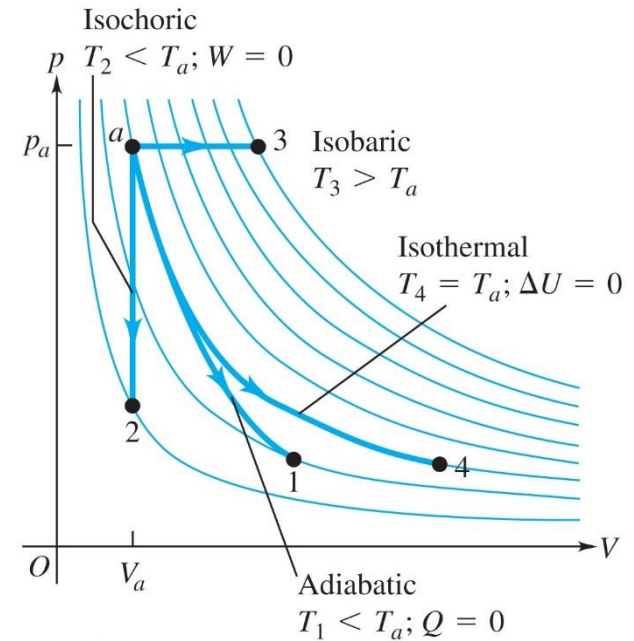
$$p = \text{constant}$$

$$W = p(V_2 - V_1)$$

- **Isothermal:** no temperature change.

$$T = \text{constant} \quad \text{or} \quad \Delta U = 0$$

$$Q = W$$



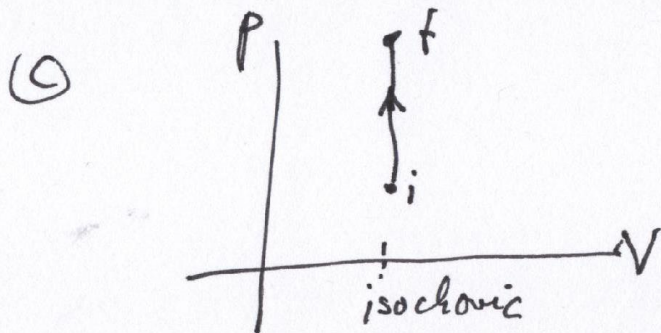
Problem 15.30

Heat capacities

- (a) How much heat does it take to increase the temperature of 2.5 moles of an ideal gas (monatomic) from 25 °C to 55 °C, if the gas is at constant volume
- (b) How much heat is needed if the gas is diatomic rather than monatomic?
- (c) Sketch in a pV diagram these processes

$$(a) Q = 2.5 \text{ mol} \frac{3}{2} (8.315 \frac{\text{J}}{\text{mol} \cdot \text{K}}) 30 \text{ K} = 935 \text{ J}$$

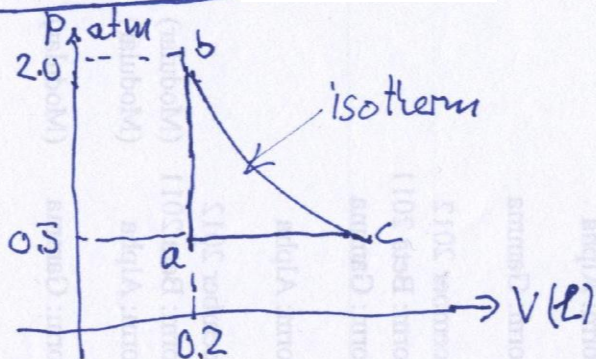
$$(b) Q = \frac{5/2}{3/2} 935 = 1560 \text{ J}$$



When the temperature increases at constant volume the pressure increases.

Problem 15.53

pV diagram for 0.004 mole of ideal H₂ gas
 Temperature does not change during bc.



- (a) What is the volume at c?
 $T_b = T_c \rightarrow$ for states b and c
 $pV = nRT \rightarrow p_b V_b = p_c V_c$
 $V_c = V_b \left(\frac{p_b}{p_c} \right) = 0.2 \frac{2}{0.5} = 0.8 \text{ L}$

note: ab isochoric (constant volume)
 bc isothermic (constant temperature)
 ca isobaric (constant pressure)

For $\Delta T = 0 \rightarrow \Delta U = 0$ and $Q = W = nRT \ln \frac{V_c}{V_b}$
 $Q = \Delta U + W$ } W isothermic
 $C_v = \frac{5}{2} R$ (diatomic gas)
 $C_p = C_v + R = \frac{7}{2} R$ $R = \frac{7}{\text{mol K}}$
 $\Delta U = n C_v \Delta T$

- (b) Find temperature of the gas at points a, b, and c.

$T_a = \frac{p_a V_a}{nR} = \frac{(0.5 \text{ atm})(1.013 \times 10^5 \text{ Pa/atm})(0.2 \times 10^{-3} \text{ m}^3)}{0.004 \text{ mol} \times 8.315 \text{ J/mol}\cdot\text{K}} = 305 \text{ K}$ [note: $P_a = \frac{N}{m^2}$]

$V_a = V_b$ for states a and b $\rightarrow T/p = V/nR \Rightarrow \text{const} \rightarrow T_a/p_a = T_b/p_b$ $T_b = T_c = T_a \frac{p_b}{p_a} = 305 \frac{2}{0.5} = 1220 \text{ K}$

- (c) continued

(c) How much heat went into or out of the gas during segments ab, ca and bc?

$$ab: Q = n C_V \Delta T = n \frac{5}{2} R \Delta T = 0.004 \text{ mol} \frac{5}{2} 8.315 \frac{\text{J}}{\text{mol} \cdot \text{K}} (1220 - 305) \text{K} = +76 \text{ J}$$

$$ca: Q = n C_p \Delta T = n \frac{7}{2} R \Delta T = 0.004 \text{ mol} \frac{7}{2} 8.315 \frac{\text{J}}{\text{mol} \cdot \text{K}} (305 - 1220) \text{K} = -107 \text{ J}$$

$$bc: Q = W = n R T \ln V_c / V_b = 0.004 \text{ mol} 8.315 \frac{\text{J}}{\text{mol} \cdot \text{K}} 1220 \text{K} \ln \left(\frac{0.8 \text{ L}}{0.2 \text{ L}} \right) = -56 \text{ J}$$

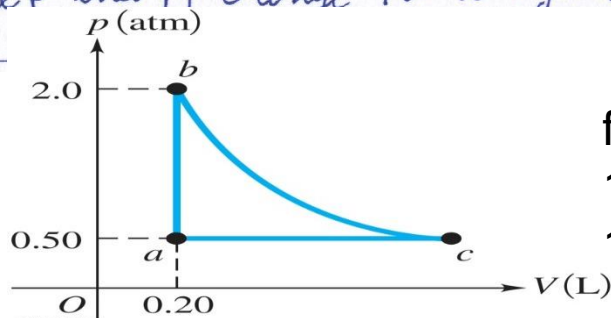
(d) Find the change in the internal energy of this hydrogen during ab, bc and ca

$$ab: \Delta U = n C_V \Delta T = n \left(\frac{5}{2} R \right) \Delta T = 0.004 \text{ mol} \frac{5}{2} 8.315 \frac{\text{J}}{\text{mol} \cdot \text{K}} (1220 - 305) = +76 \text{ J}$$

$$bc: \Delta T = 0 \rightarrow \Delta U = 0$$

$$ca: \Delta U = p(V_c - V_a) + n(7/2R)\Delta T = (0.5)(1.013 \cdot 10^5)(.8 - .2)(10^{-3}) + 0.004 \left(\frac{7}{2} * 8.31 \right) (305 - 1220) = 76 \text{ J}$$

note: the net energy change in a cycle is zero: $\Delta U_{\text{total}} = +76 + 0 - 76 = 0$



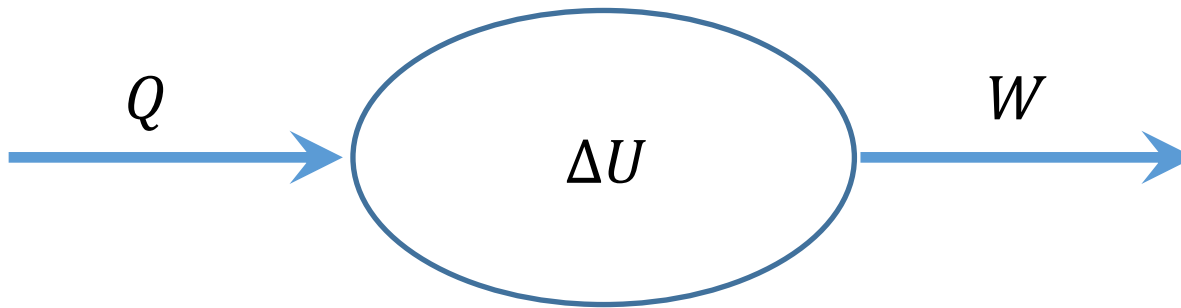
factors of unity

$$1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$$

$$1 \text{ liter} = 1000 \text{ cm}^3 = 10^{-3} \text{ m}^3$$

15.5 The First Law of Thermodynamics

It sets the relationship between the change in the internal energy ΔU , work done by the system W , and heat transfer.



$$\Delta U = Q - W$$

Note: (a) Q is positive if added to the system; negative if removed from the system.
(b) W is positive if it is done by the system on the surrounding; negative otherwise.

Work done during volume change

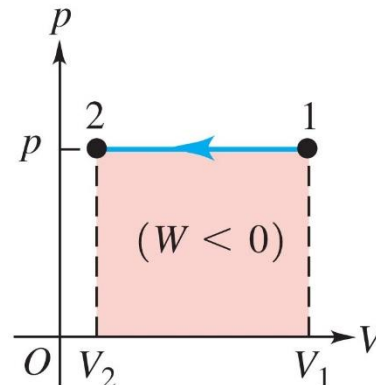
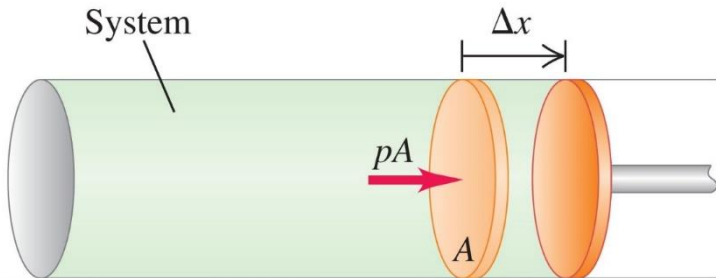
$$\text{Work: } W = F\Delta x = pA\Delta x = p\Delta V$$

$$\text{Work done at constant pressure: } W = p(V_2 - V_1)$$

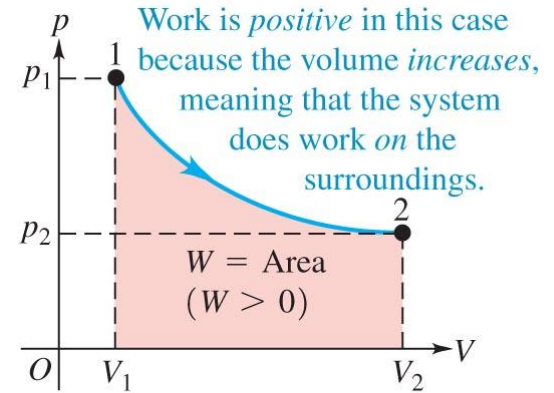
When the pressure is not a constant:

$$W = p_1\Delta V + p_2\Delta V + p_3\Delta V + \dots$$

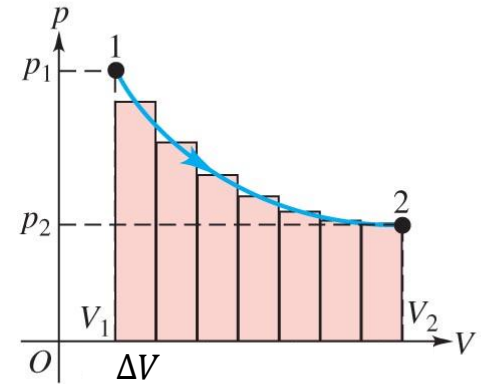
which is the area under the pV diagram



Constant pressure



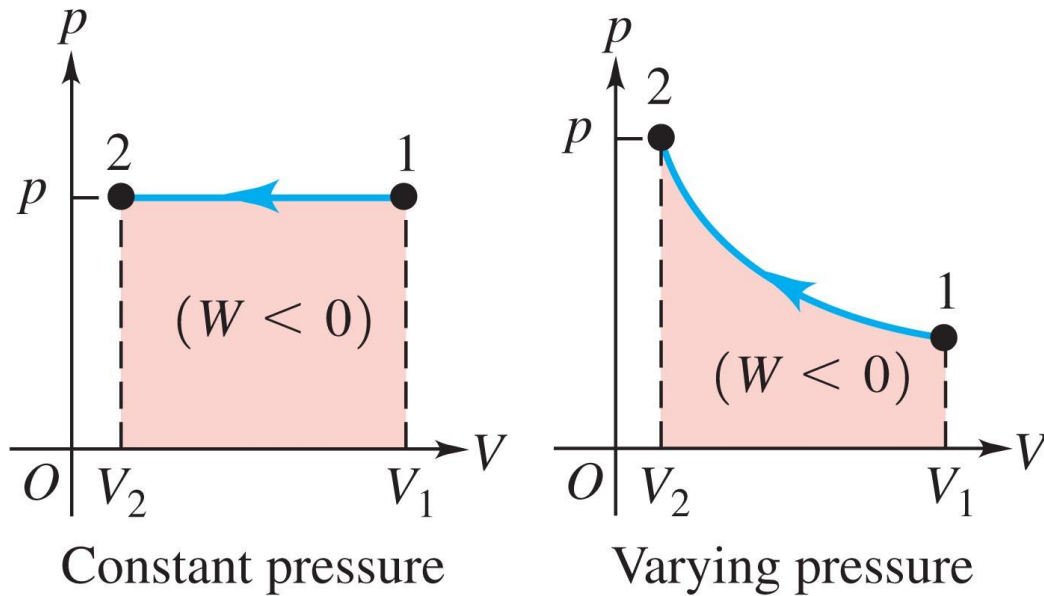
(a) pV diagram for a system undergoing a change in volume with varying pressure



(b) The curve in (a) treated as a series of small constant-pressure intervals

Work is the area under the pV diagram

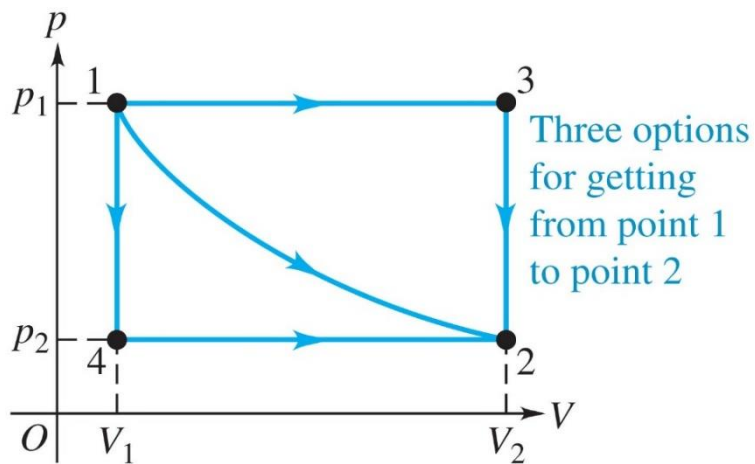
The volume *decreases* ($V_2 < V_1$) and the system does negative work.



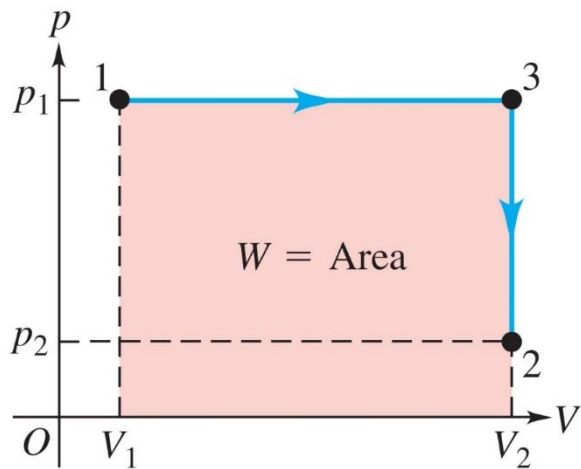
Work done at constant temperature

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

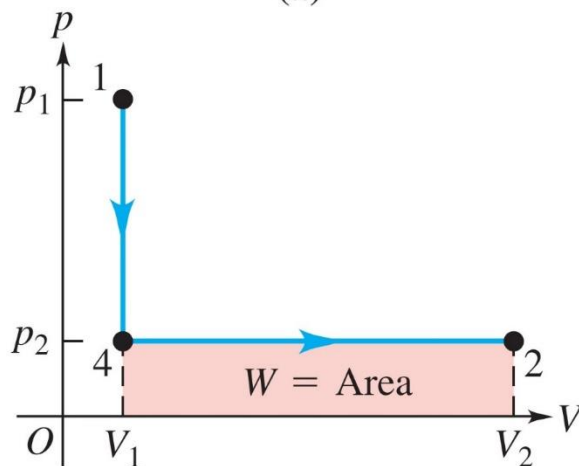
Work is the area under the pV diagram.
It depends on the exact path that the system follows.



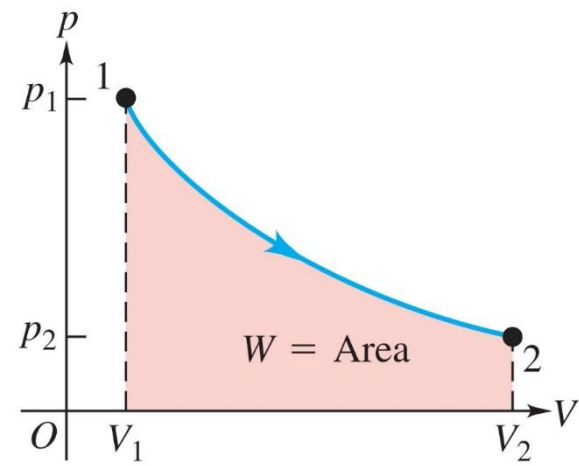
(a)



(b)



(c)



(d)

Example 15.10 on page 483

Given:

- (1) from a to b, $Q_{ab} = 150 \text{ J}$ of heat is added to the system
- (2) From b to d, $Q_{bd} = 600 \text{ J}$ of heat is added to the system

- Find:
- (1) internal energy change from a to b
 - (2) internal energy change from a to b to d
 - (3) total heat added to system from a to c to d

Solution:

(1) From a to b $W = 0$ $\Delta U_{ab} = Q_{ab} - W = 150 \text{ J}$

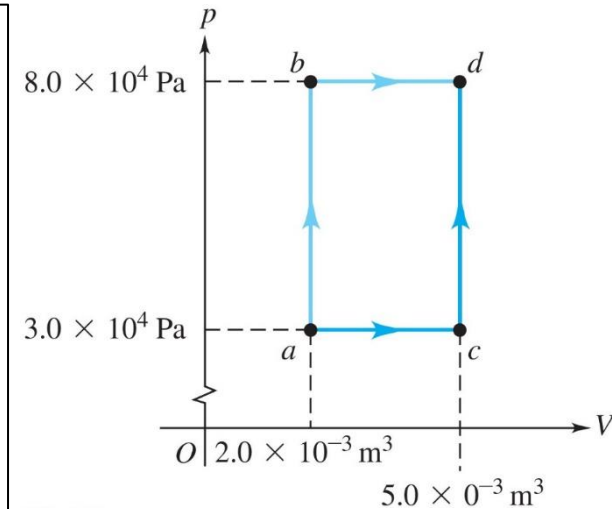
- (1) From b to d, constant pressure,

$$W_{bd} = p(V_d - V_b) = (8.0 \times 10^4)(5.0 \times 10^{-3} - 2.0 \times 10^{-3}) = 240 \text{ J}$$

J

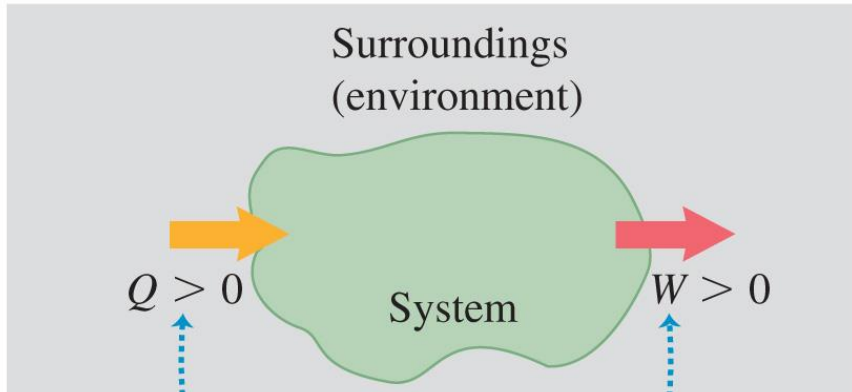
$$\Delta U_{abd} = Q_{abd} - W_{abd} = (150 + 600) - (0 + 240) = 510 \text{ J}$$

(3) $Q_{acd} = \Delta U_{acd} + W_{acd} = \Delta U_{abd} + W_{ac}$
 $= 510 + (3.0 \times 10^4)(5.0 \times 10^{-3} - 2.0 \times 10^{-3}) = 510 + 90 = 600 \text{ J}$



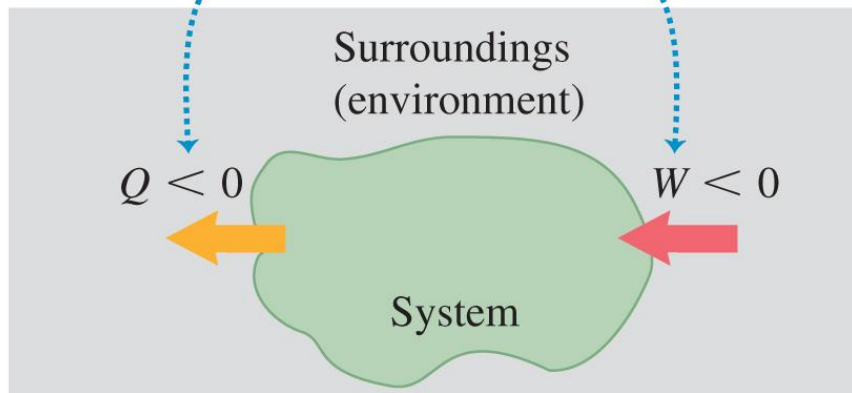
The First Law
 $\Delta U = Q - W$

Energy, heat, and work in a thermodynamic system: The first law of Thermodynamics



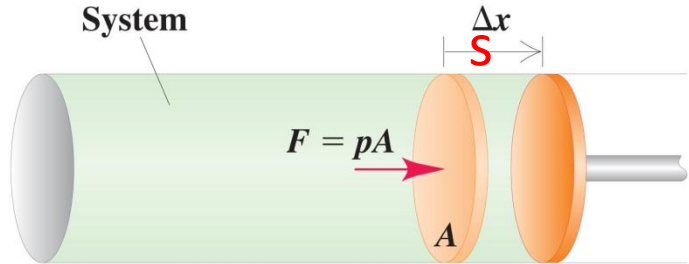
Heat is positive when it *enters* the system, negative when it *leaves* the system.

Work is positive when it is done *by* the system, negative when it is done *on* the system.



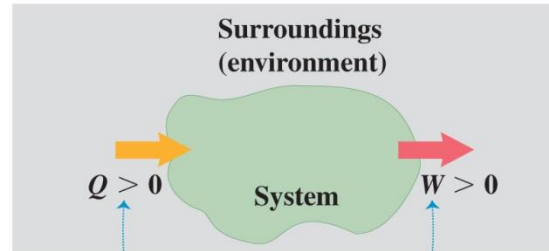
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Work done during volume changes

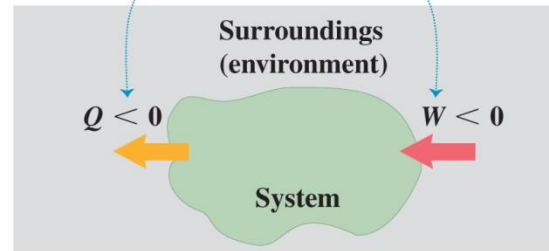


Thermodynamics is the study of Energy, *heat* and *Work*
 Q added \uparrow W done
 (sign convection)

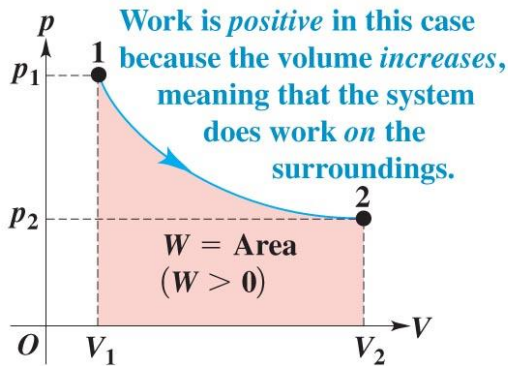
Thermodynamic system = exchanges heat with environment



Heat is positive when it enters the system, negative when it leaves the system.
 Work is positive when it is done by the system, negative when it is done on the system.

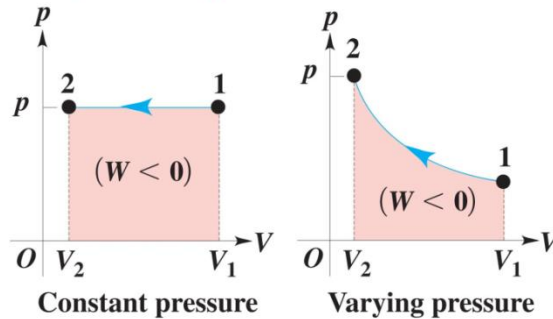


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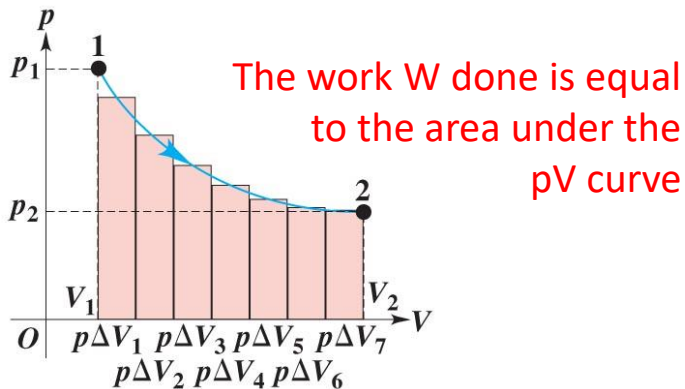


(a) pV diagram for a system undergoing a change in volume with varying pressure

The volume *decreases* ($V_2 < V_1$), meaning that the surroundings do work on the system. Thus, work is *negative*.



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(b) The curve in (a) treated as a series of small constant-pressure intervals

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Work done during volume changes

When gas expands, it pushes on the boundary surfaces and does positive work.

$$W = F\Delta x = p \underbrace{A\Delta x}_{\Delta V} = p\Delta V$$

Assume p is constant;

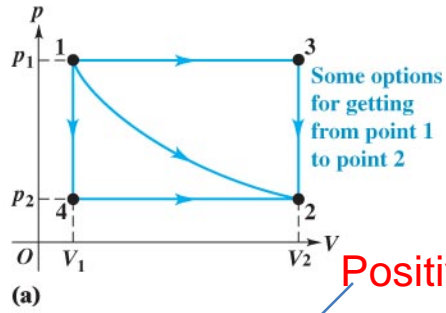
$$W = p(V_2 - V_1)$$

But usually it is not constant;

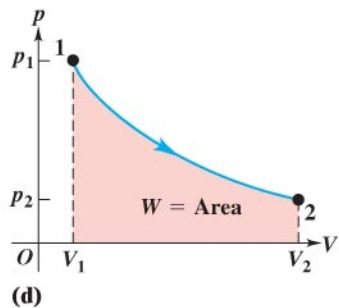
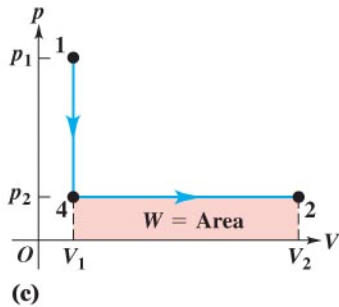
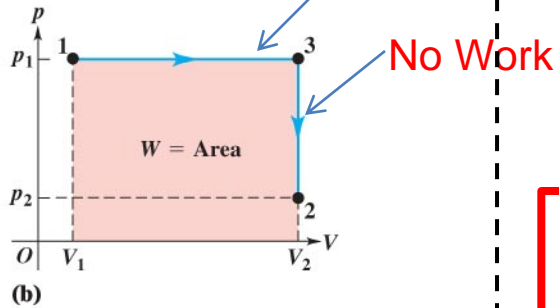
$$W = p_1\Delta V_1 + p_2\Delta V_2 \dots \dots$$

Isothermal (constant temperature) expansion (Particular case)

$$W = nRT \ln \frac{V_2}{V_1} \text{ (without proof)}$$



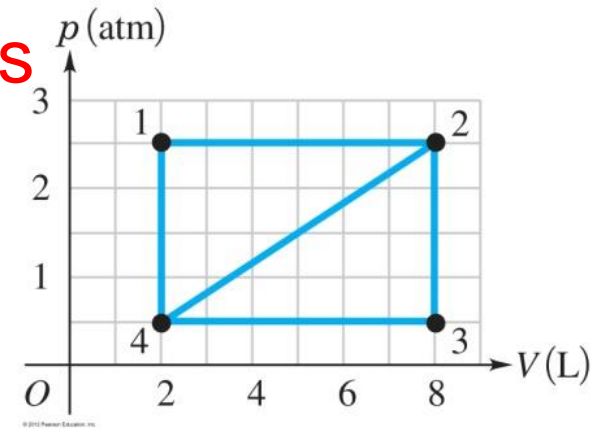
Positive work



Consider a series of paths, in such a way that each can be plotted on a pV-diagram → they all require different work (areas under the path)

Work done depends not only on the initial and final points, but also on the path taken.

Work done in a cyclic process



15.39 note:

For a constant volume process: $W=0$

For a constant pressure process: $W=p \cdot \Delta V$

1 atm = $1.013 \times 10^5 \text{ Pa}$, 1 Liter = 10^{-3} m^3

The work done is positive when the volume increases and negative when the volume decreases.

Find W for each process in the cycle;

$$1 \rightarrow 2: W = p \Delta V = 2.5 \text{ atm} * 1.013 \times 10^5 \frac{\text{Pa}}{\text{atm}} (8\text{L} - 2\text{L}) \times 10^{-3} \frac{\text{m}^3}{\text{L}} = 1.5 \times 10^3 \text{ J}$$

$$2 \rightarrow 3: W = 0 \text{ since } \Delta V = 0$$

$$3 \rightarrow 4: W = p \Delta V = 0.5 \text{ atm} * 1.013 \times 10^5 \frac{\text{Pa}}{\text{atm}} (2\text{L} - 8\text{L}) \times 10^{-3} \frac{\text{m}^3}{\text{L}} = -3.0 \times 10^2 \text{ J}$$

$$4 \rightarrow 1: W = 0 \text{ since } \Delta V = 0$$

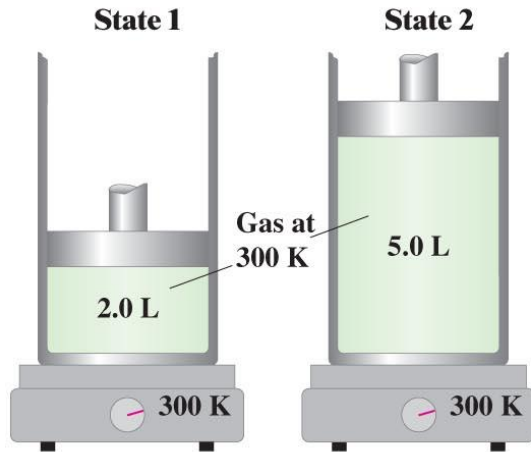
$$W_{\text{cycle}} = 1.5 \times 10^3 \text{ J} + 0 + (-3.0 \times 10^2 \text{ J}) + 0 = 1.2 \times 10^3 \text{ J}$$

The area enclosed by the cycle (energy) is;

$$2 \text{ atm} * 6 \text{ L} \cong 12.0 \text{ L} \cdot \text{atm} * 10^{-3} \frac{\text{m}^3}{\text{L}} * 1.013 \times 10^5 \frac{\text{Pa}}{\text{atm}} = 1.2 \times 10^3 \text{ J}$$

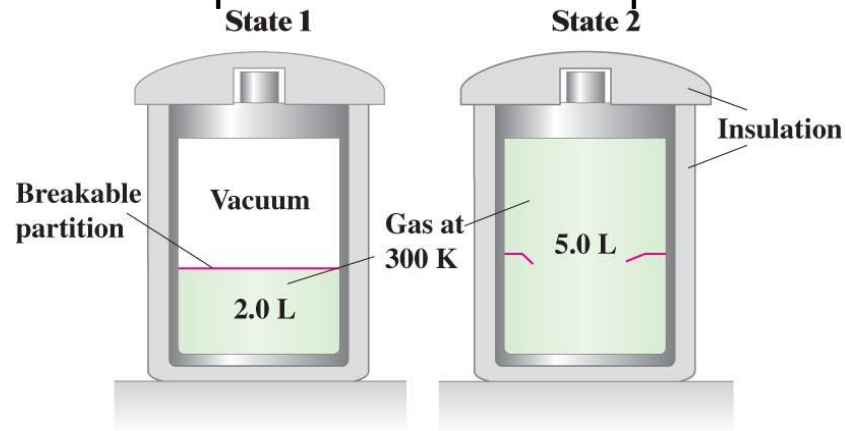
Heat transfer during volume changes

Slow controlled isothermal expansion Rapid uncontrolled expansion



(a) System does work on piston; hot plate adds heat to system ($W > 0$ and $Q > 0$).

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(b) System does no work; no heat enters or leaves system ($W = 0$ and $Q = 0$).

Free expansion=uncontrolled expansion

Experiments have shown that during free expansion, there is no change in temperature. Heat also depends on the path like work.

Q = heat of an object is not a useful concept, better talk about internal energy U

First law of thermodynamics

$$\begin{array}{ccccc}
 Q & = & \Delta U & + & W \\
 \uparrow & & \uparrow & & \uparrow \\
 \text{Added} & & \text{Change of} & & \text{Work done} \\
 \text{heat} & & \text{internal energy} & & \text{against surroundings}
 \end{array}$$

Experiments show $U=f(p,V,T)$

$$U_2 - U_1 = \underbrace{\Delta U}_{\text{independent of path}} = Q - W$$

Example

One gram of water (1cm^3) becomes 1671cm^3 steam when boiled at constant pressure of 1atm . The heat of vaporization is $L_V = 2.256 \times 10^6 \frac{\text{J}}{\text{kg}}$

Compute: (a) the work done by the water when it vaporizes
(b) the increase in internal energy

$$(a) W = p(V_2 - V_1) = 1.013 \times 10^5 \text{Pa} (1671 \times 10^{-6} \text{m}^3 - 1 \times 10^{-6} \text{m}^3) = 169 \text{ J}$$

$$(b) Q = mL_o = 1g * 2256 \frac{\text{J}}{\text{g}} = 2256 \text{ J}$$

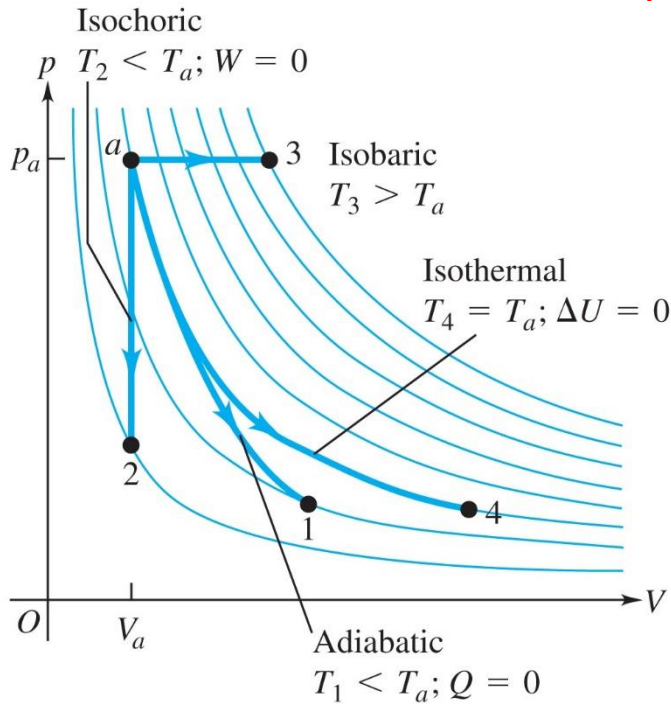
First law of thermodynamics: $Q = \Delta U + W$

$$\Delta U = Q - W = (2256 - 169) \text{J} = 2087 \text{ J}$$

Why is $\Delta U > W$??

Not all heat goes into internal energy but some heat does work on the water molecules pulling them apart when water transforms into steam.

Thermodynamic processes



4 processes:

- No heat transfer = Adiabatic
- Constant volume = isochoric
- Constant pressure = isobaric
- Constant temperature = isothermal

Isothermal: $\rightarrow \Delta T = 0, \Delta U = 0 \quad W=Q$

Adiabatic: $\rightarrow Q=0$

$$\Delta U = U_2 - U_1 = Q - W = -W$$

$$\begin{array}{c} || \\ 0 \end{array}$$

Expanding system $W > 0, \Delta U < 0$

Compressing system $W < 0, \Delta U > 0$

Increasing internal energy is often happen with increasing temperature T

Example: combustion engine; **isochoric** \rightarrow constant volume

$$U_2 - U_1 = \Delta U = Q - W$$

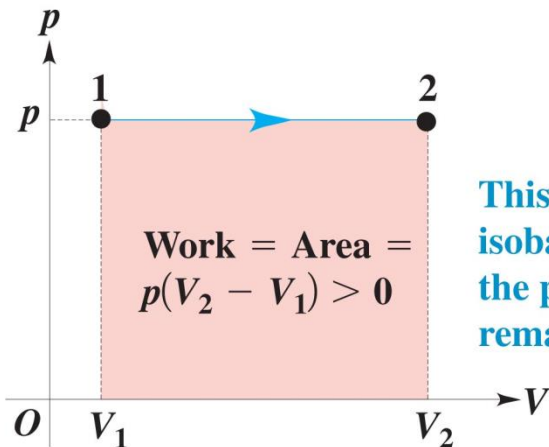
$$\begin{array}{c} || \\ 0 \end{array}$$

All the energy added as heat increases energy U

Example: heating a gas in a closed volume **isobaric** \rightarrow constant pressure

All three quantities $\Delta U_1, W_1, \text{ and } Q$ change

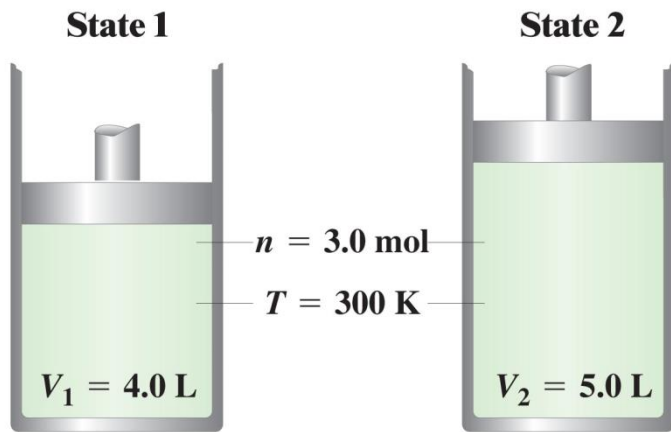
$$W = p(V_2 - V_1) \quad Q = nC_p\Delta T \quad \Delta U = Q - W$$



This process is isobaric because the pressure remains constant.

Constant pressure isobaric \rightarrow constant pressure: none of the quantities $\Delta U_1, W_1, \text{ and } Q$ is zero.

Example 15.9 An isothermal expansion



Example 15.9

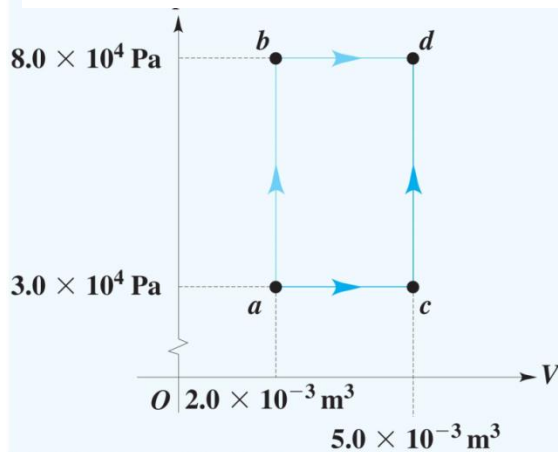
$$W = nRT \ln \frac{V_2}{V_1} = 3 \text{ mol} * 8.3 \frac{\text{J}}{\text{mol} \cdot \text{K}} * 300 \text{ K} * \ln \frac{5 \text{ L}}{4 \text{ L}} = 1700 \text{ J}$$

Since, temperature is constant and we consider an ideal gas the change in internal energy is zero \rightarrow all the heat entering goes into work



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Example 15.10 A series of thermodynamical processes (due to its importance repeated)



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Consider paths in a **pV** diagram: in path **ab** 150J of heat are added to the system, in **bd**. 600J of heat are added. Find

- Internal energy change in **ab** ?
- Internal energy change in **abd** ?
- Total heat added in **acd** ?

- No volume change $\rightarrow W_{ab} = 0$, $\Delta U_{ab} = Q_{ab} = 150 \text{ J}$
- bd** at constant pressure

$$W_{bd} = p(V_2 - V_1) = 8 \times 10^4 \text{ Pa} (5 - 2) \times 10^{-3} \text{ m}^3 = 240 \text{ J}$$

$$W_{total} = W_{ab} + W_{bd} = 0 + 240 = 240 \text{ J}$$

$$Q_{abd} = Q_{ab} + Q_{bd} = 150 + 600 = 750 \text{ J}$$

$$\Delta U_{abd} = Q_{abd} - W_{abd} = 750 - 240 = 510 \text{ J}$$

- Because ΔU is independent of the path $\Delta U_{acd} = \Delta U_{abd}$

Total work for path **acd**:

$$W_{total} = W_{ac} + W_{cd} = p(V_2 - V_1) + 0 = 3 \times 10^4 \text{ Pa} (5 - 2) \times 10^{-3} \text{ m}^3 = 90 \text{ J}$$

Problem on Heat Capacities

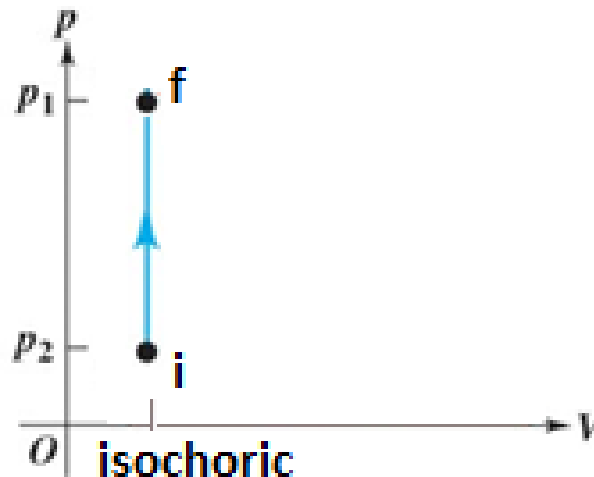
- How much heat does it take to increase the temperature of 2.5 moles of an ideal gas (monoatomic) from 25°C to 55°C, if the gas is at constant volume.
- How much heat is needed if the gas is diatomic rather than monoatomic?
- Sketch in a **pV**-diagram of these processes.

a) $Q = 2.5 \text{ mol} \frac{3}{2} \left(8.315 \frac{\text{J}}{\text{mol.K}} \text{C} \right) 30 \text{K} = 935 \text{J}$

$$R = 8.315 \frac{\text{J}}{\text{mol.K}} \text{C}$$

b) $Q = \frac{5/2}{3/2} * 935 = 1560 \text{J}$

c)



Isochoric = when the temperature increases at constant volume the pressure increases

Glicker - Questions 3

You compress a sample of air slowly to half its original volume, keeping its temperature constant. The internal energy of the gas.

- A. Decreases to half its original value.
- B. Remains unchanged.
- C. Increases to twice its original value.

15.7 Properties of an Ideal Gas

$$\Delta U = Q - W$$

We learned in Section 15.4 that the constant-volume molar heat capacity for a monatomic ideal gas is

$$C_V = \frac{3}{2}R = 12.5 \text{ J/(mol}\cdot\text{K)}$$

Question: What is the molar heat capacity for a monatomic ideal gas under a constant pressure? [$p = \text{constant}$; $W = p(V_2 - V_1) = p\Delta V$]

$$Q = \Delta U + W = nC_V\Delta T + p\Delta V$$

Since $pV = nRT$, or $p\Delta V = nR\Delta T$

We have

$$Q = nC_V\Delta T + p\Delta V = nC_V\Delta T + nR\Delta T = n(C_V + R)\Delta T = nC_p\Delta T.$$

The constant-pressure molar heat capacity is $C_p = C_V + R = \frac{5}{2}R$

Properties of an ideal gas: Heat capacities and the adiabatic process

Free expansion: When the partition is broken the gas expands freely into the vacuum region. Internal energy stays constant and temperature does not change

Molar heat capacity depends on condition under which heat is added.

C_V = heat is added to raise temperature $Q = \Delta U$ under constant volume, but letting pressure go up.

C_p = heat is added while gas expands $Q = \Delta U + W$ but keeping pressure constant.

Adiabatic: $Q=0$

$$p_1 V_1^\gamma = p_2 V_2^\gamma = \text{constant} \rightarrow \gamma = \frac{C_p}{C_V}$$

Isothermal: $\Delta T=0$

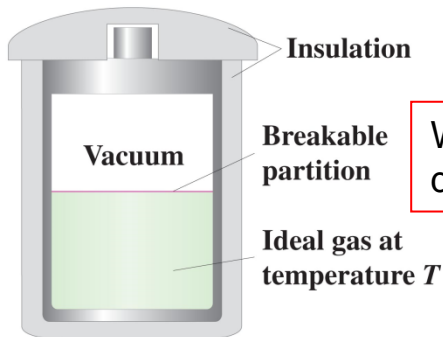
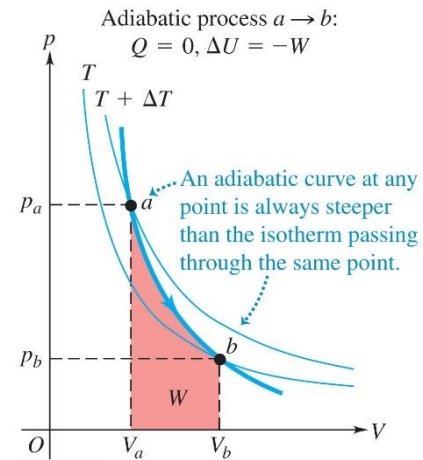
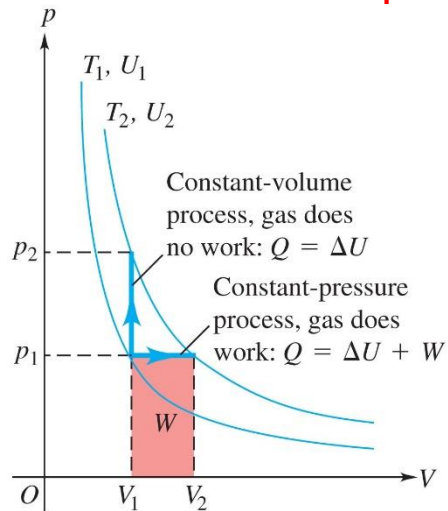
$$p_1 V_1 = p_2 V_2 = nRT$$

TABLE 15.4 Molar heat capacities of gases at low pressure

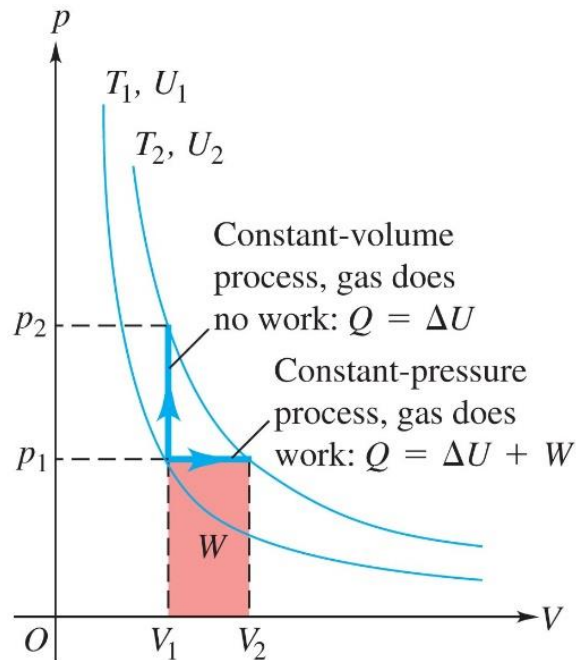
Type of gas	Gas	C_V (J/(mol · K))	C_p (J/(mol · K))	$C_p - C_V$ (J/(mol · K))	γ
Monatomic	He	12.47	20.78	8.31	1.67
	Ar	12.47	20.78	8.31	1.67
Diatomic	H ₂	20.42	28.74	8.32	1.41
	N ₂	20.76	29.07	8.31	1.40
	O ₂	20.85	29.17	8.31	1.40
	CO	20.85	29.16	8.31	1.40
Polyatomic	CO ₂	28.46	36.94	8.48	1.30
	SO ₂	31.39	40.37	8.98	1.29
	H ₂ S	25.95	34.60	8.65	1.33

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Note: $C_p = C_V + R$ where $R = 8.314 \frac{J}{mol \cdot K}$



Walls of container do not move



Molar heat capacity depends on condition under which heat is added.

C_V = heat is added to raise temperature $Q = \Delta U$ under constant volume, but letting pressure go up. $W=0$ no work, since volume is constant.

C_p = heat is added while gas expands $Q = \Delta U + W$ but keeping pressure constant. $W > 0$ work performed, since volume is expanding

$$C_p = C_V + R \text{ where } R = 8.314 \frac{J}{mol.K}$$

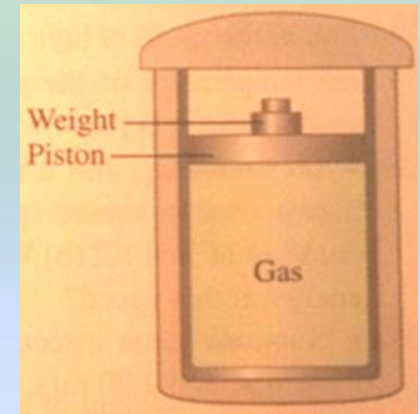
Careful with **constant pressure equations** $W = p\Delta V = nR \Delta T$

$\Delta U = nC_V\Delta T$, if at constant pressure replace $C_V = C_p - R = 3/2R$ for a mono atomic gas

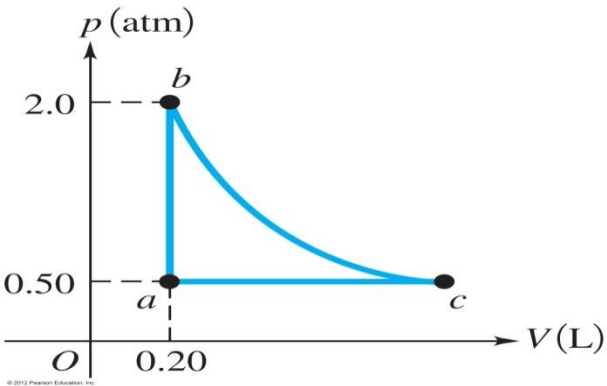
Gicker - Questions 4

The gas shown in figure is in a completely insulated rigid container. Weight is added to the frictionless piston, compressing the gas. As this is done,

- A. The temperature of the gas stays the same because the container is insulated.
- B. The temperature of the gas increases because heat is added to the gas.
- C. The temperature of the gas increases because work is done on the gas.
- D. The pressure of the gas stays the same because the temperature of the gas is constant.



Problem 15 - 75



Note: **ab** isochoric (constant volume)

bc isothermic (constant temperature)

ca isobaric (constant pressure)

For;

$$\left. \begin{array}{l} \Delta T = 0 \rightarrow \Delta U = 0 \\ Q = \Delta U + W \end{array} \right\} Q = W = nRT \ln \frac{V_c}{V_b} \text{ (isotherm)}$$

$$C_V = \frac{5}{2}R \text{ (diatomic gas)}$$

$$C_p = C_V + R = \frac{7}{2}R \quad (R=8.315 \frac{J}{mol.K})$$

$$\Delta U = nC_V\Delta T$$

(a) What is the volume at **c** ?

$T_b = T_c \rightarrow$ for states **b** and **c**

$$pV = nRT \rightarrow p_b V_b = p_c V_c$$

$$V_c = V_b \left(\frac{p_b}{p_c} \right) = 0.2 * \frac{2}{0.5} = 0.8 \text{ L}$$

(b) Find temperature of the gas at points **ab** and **c**

$$T_a = \frac{p_a V_a}{nR} = \frac{(0.5 \text{ atm})(1.013 \times 10^5 \frac{Pa}{atm})(0.2 \times 10^{-3} \text{ m}^3)}{0.004 \text{ mol} * 8.315 \frac{J}{\text{mol.K}}} = 305 \text{ K} \text{ (Note: } p_a = \frac{N}{\text{m}^2}\text{)}$$

$$V_a = V_b \rightarrow \text{for states } \mathbf{a} \text{ and } \mathbf{b} \rightarrow \frac{T}{p} = \frac{V}{nR} = \text{constant} \rightarrow \frac{T_a}{p_a} = \frac{T_b}{p_b}$$

$$T_b = T_c = T_a \frac{p_b}{p_a} = 305 * \frac{2}{0.5} = 1220 \text{ K}$$

pV-diagram for 0.004mole of ideal H₂ gas
temperature does not change during path **bc**.

Continued on next slide

(c) How much heat went into or out of the gas during segments **ab**, **ca** and **bc** ?

$$\mathbf{ab}: Q = nC_V\Delta T = n\frac{3}{2}R\Delta T = (0.004\text{mol})\frac{3}{2} * 8.315 \frac{\text{J}}{\text{mol.K}} (1220 - 305)\text{K} = +76 \text{ J}$$

$$\mathbf{ca}: Q = nC_p\Delta T = n\frac{7}{2}R\Delta T = (0.004\text{mol})\frac{7}{2} * 8.315 \frac{\text{J}}{\text{mol.K}} (305 - 1220)\text{K} = -107 \text{ J}$$

$$\mathbf{bc}: Q = W = nRT = nRT\ln\frac{V_c}{V_b} = (0.004\text{mol}) * 8.315 \frac{\text{J}}{\text{mol.K}} \left(1220\text{K} * \ln\left(\frac{0.8\text{L}}{0.2\text{L}}\right)\right) = +56 \text{ J}$$

(d) Find the change in the internal energy of this hydrogen during segments **ab**, **ca** and **bc** ?

$$\mathbf{ab}: \Delta U = nC_V\Delta T = n\frac{5}{2}R\Delta T = (0.004\text{mol})\frac{5}{2} * 8.315 \frac{\text{J}}{\text{mol.K}} (1220 - 305)\text{K} = +76 \text{ J}$$

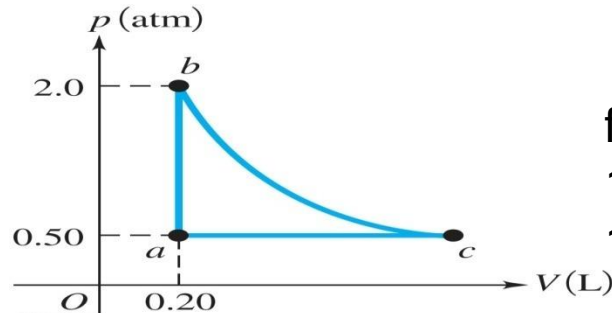
$$\mathbf{ca}: \Delta U = p(V_c - V_a) + n\frac{7}{2}R\Delta T$$

$$= 0.5 * 1.013 * 10^5 (0.8 - 0.2) * 10^{-3} + (0.004\text{mol})\frac{7}{2} * 8.315 \frac{\text{J}}{\text{mol.K}} (305 - 1220)\text{K}$$

$$= -76 \text{ J}$$

$$\mathbf{bc}: \Delta T = 0 \rightarrow \Delta U = 0$$

Note: the net energy change in a cycle is zero. $\Delta U_{total} = +76 + 0 - 76 = 0$



factors of unity

$$1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$$

$$1 \text{ m}^3 = 10^3 \text{ L}$$

70. II Helium gas expands slowly to twice its original volume, doing 300 J of work in the process. Find the heat added to the gas and the change in the internal energy of the gas if the process is (a) isothermal and (b) adiabatic.

15.70. Set Up: For an isothermal process, $\Delta T = 0$. For an adiabatic process, $Q = 0$.

Solve: (a) $\Delta T = 0$. $\Delta U = 0$ and $Q = W = 300$ J

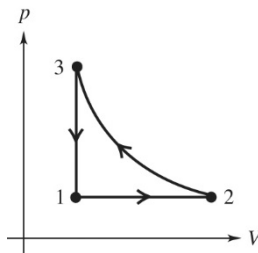
(b) $Q = 0$. $\Delta U = -W = -300$ J

71. II A cylinder with a piston contains 0.250 mol of ideal oxygen at a pressure of 2.40×10^5 Pa and a temperature of 355 K. The gas first expands isobarically to twice its original volume. It is then compressed isothermally back to its original volume, and finally it is cooled isochorically to its original pressure. (a) Show the series of processes on a pV diagram. (b) Compute the temperature during the isothermal compression. (c) Compute the maximum pressure. (d) Compute the total work done by the piston on the gas during the series of processes.

15.71. Set Up: $pV = nRT$. For the isobaric process, $W = p \Delta V = nR \Delta T$. For the isothermal process,

$$W = nRT \ln \left(\frac{V_f}{V_i} \right)$$

Solve: (a) The pV diagram for these processes is sketched in the figure below.



(b) Find T_2 . For process $1 \rightarrow 2$, n , R , and p are constant so $\frac{T}{V} = \frac{p}{nR} = \text{constant}$. $\frac{T_1}{V_1} = \frac{T_2}{V_2}$ and

$$T_2 = T_1 \left(\frac{V_2}{V_1} \right) = (355 \text{ K})(2) = 710 \text{ K}$$

(c) The maximum pressure is for state 3. For process $2 \rightarrow 3$, n , R , and T are constant. $p_2 V_2 = p_3 V_3$ and

$$p_3 = p_2 \left(\frac{V_2}{V_3} \right) = (2.40 \times 10^5 \text{ Pa})(2) = 4.80 \times 10^5 \text{ Pa}$$

(d) process $1 \rightarrow 2$: $W = p \Delta V = nR \Delta T = (0.250 \text{ mol})(8.315 \text{ J/mol} \cdot \text{K})(710 \text{ K} - 355 \text{ K}) = 738 \text{ J}$.

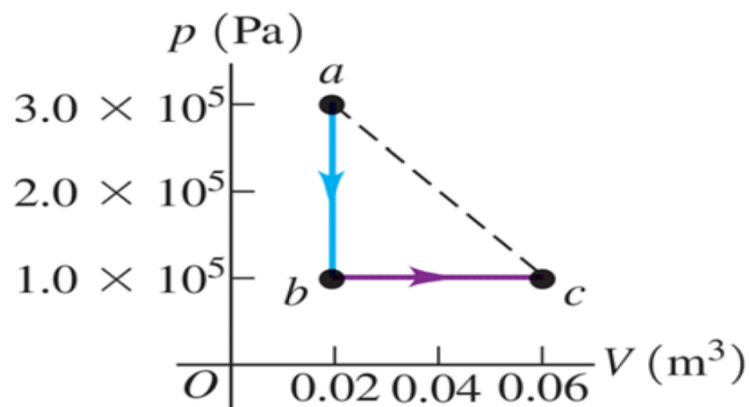
$$\text{process } 2 \rightarrow 3: W = nRT \ln \left(\frac{V_3}{V_2} \right) = (0.250 \text{ mol})(8.315 \text{ J/mol} \cdot \text{K})(710 \text{ K}) \ln \left(\frac{1}{2} \right) = -1023 \text{ J}.$$

process $3 \rightarrow 1$: $\Delta V = 0$ and $W = 0$.

The total work done is $738 \text{ J} + (-1023 \text{ J}) = -285 \text{ J}$. This is the work done by the gas. The work done on the gas is 285 J.

- 52. II** A volume of air (assumed to be an ideal gas) is first cooled without changing its volume and then expanded without changing its pressure, as shown by the path abc in **Figure 15.35**. (a) How does the final temperature of the gas compare with its initial temperature? (b) How much heat does the air exchange with its surroundings during the process abc ? Does the air absorb heat or release heat during this process? Explain. (c) If the air instead expands from state a to state c by the straight-line path shown, how much heat does it exchange with its surroundings?

Figure 15.35



15.52. Set Up: Use $pV = nRT$ to calculate T_c/T_a . Calculate ΔU and W and use $\Delta U = Q - W$ to obtain Q . For path ac , the work done is the area under the line representing the process in the pV diagram.

Solve: (a)
$$\frac{T_c}{T_a} = \frac{p_c V_c}{p_a V_a} = \frac{(1.0 \times 10^5 \text{ J})(0.060 \text{ m}^3)}{(3.0 \times 10^5 \text{ J})(0.020 \text{ m}^3)} = 1.00. \quad T_c = T_a.$$

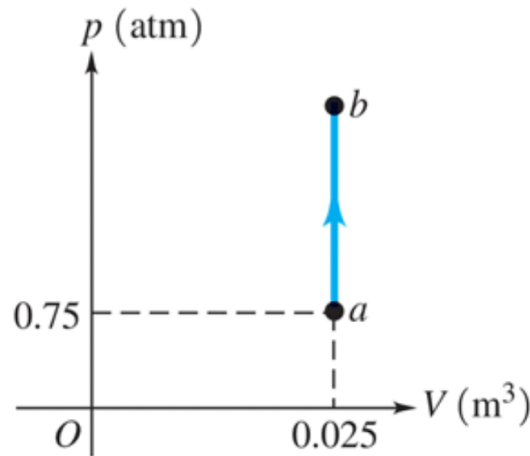
(b) Since $T_c = T_a$, $\Delta U = 0$ for process abc . For ab , $\Delta V = 0$ and $W_{ab} = 0$. For bc , p is constant and $W_{bc} = p\Delta V = (1.0 \times 10^5 \text{ Pa})(0.040 \text{ m}^3) = 4.0 \times 10^3 \text{ J}$. Therefore, $W_{abc} = +4.0 \times 10^3 \text{ J}$. Since $\Delta U = 0$, $Q = W = +4.0 \times 10^3 \text{ J}$. $4.0 \times 10^3 \text{ J}$ of heat flows into the gas during process abc .

(c)
$$W = \frac{1}{2}(3.0 \times 10^5 \text{ Pa} + 1.0 \times 10^5 \text{ Pa})(0.040 \text{ m}^3) = +8.0 \times 10^3 \text{ J}. \quad Q_{ac} = W_{ac} = +8.0 \times 10^3 \text{ J}.$$

Reflect: The work done is path dependent and is greater for process ac than for process abc , even though the initial and final states are the same.

49. II **Figure 15.32** shows a pV diagram for an ideal gas in which its pressure tripled from a to b when 534 J of heat was put into the gas. (a) How much work was done by the gas between a and b ? (b) Without doing any calculations, decide whether the temperature of this gas increased, decreased, or remained the same between a and b . Explain your reasoning. (c) By how much did the internal energy of the gas change between a and b ? Did it increase or decrease? (d) What is the temperature of the gas at point b in terms of its temperature at a , T_a ?

Figure 15.32



15.49. Set Up: The pV diagram shows that V is constant during the process.

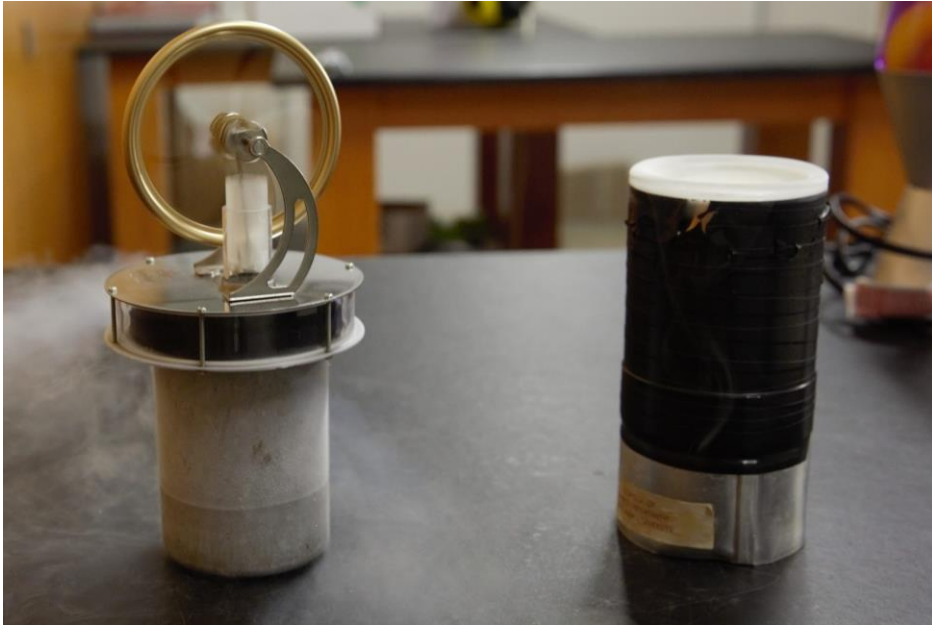
Solve: (a) $W = 0$ since $\Delta V = 0$.

(b) $pV = nRT$ and $T = \left(\frac{V}{nR}\right)p$. When p increases while V and n are constant, then T must increase. In fact, if p triples the absolute temperature T triples.

(c) $\Delta U = Q - W$. $Q = +534$ J and $W = 0$ gives $\Delta U = +534$ J. The internal energy increased by 534 J.

(d) $T_b = 3T_a$, as derived in part (b).

Stirling Engine



The Stirling Engine is a piston that, when heated or cooled, increases or decreases the pressure/energy of the gas trapped inside. This causes the gas molecules to apply more pressure on the piston. This in turn increases the pressure on the opposite side of the piston, and the cycle repeats. As long as heat is allowed to flow (be it from a cold or hot source) the gas pressure variance will drive the piston.

To set up the demonstration, place the beaker of water on the hot plate and the stirling engine on the beaker. Turn the hot plate on to 300C. It will take approximately 21 minutes for the water to boil. If the stirling engine does not begin to spin on its own, give it a small spin.

Crookes Radiometer



The radiometer consists of black and white vanes inside a partial vacuum. When heated via a light bulb, the vanes begin to spin (Black vanes leading, or clockwise in the photo) due to thermal transpiration as well as gas pressure differential.