

Ideal Gases

Given the typically large numbers of atoms or molecules within a small volume of gas, quantitative descriptions are usually in terms of macroscopic parameters: temperature, volume, and pressure versus a microscopic treatment of individual atom dynamics.

An equation of state interrelates these macroscopic parameters in a single equation. An ideal gas is a low-density gas at high temperature where intermolecular interactions and the volume of the gas molecules are negligible.

The equation of state for an ideal gas is:

$$PV = NkT \quad \text{Or} \quad PV = nRT$$

$$P = \textit{pressure} \quad Pa$$

$$V = \textit{volume} \quad m^3$$

$$N = \# \textit{ particles} \quad n = \# \textit{ moles}$$

$$T = \textit{temperature} \quad \textit{kelvin}$$

$$k = \textit{ Boltzmann } _ \textit{ Const.} \quad 1.38 \times 10^{-23} \textit{ J / K}$$

$$R = \textit{ Universal } _ \textit{ Gas } _ \textit{ Const.} \quad 8.31 \textit{ J / mole} \cdot \textit{ K}$$

One mole of a substance equals 6.02×10^{23} units of the substance and is equal in weight to the substance gram molecular weight [GMW].

Avogadro's number is 6.02×10^{23} molecules / mole.

As an example, one mole of H_2 gas is 2 grams and has 6.02×10^{23} H_2 molecules.

In addition, the **volume of 1mole of any gas at STP [1ATM and 273.15 K] is $22.4 \times 10^{-3} \text{ m}^3 = 22.4 \text{ L}$.**

Non-ideal Gas

When intermolecular interactions and the volume of the molecules are included in the equation of state, the result is the van der Waals equation:

$$\left(p + \frac{an^2}{V^2} \right) * (V - nb) = nRT$$

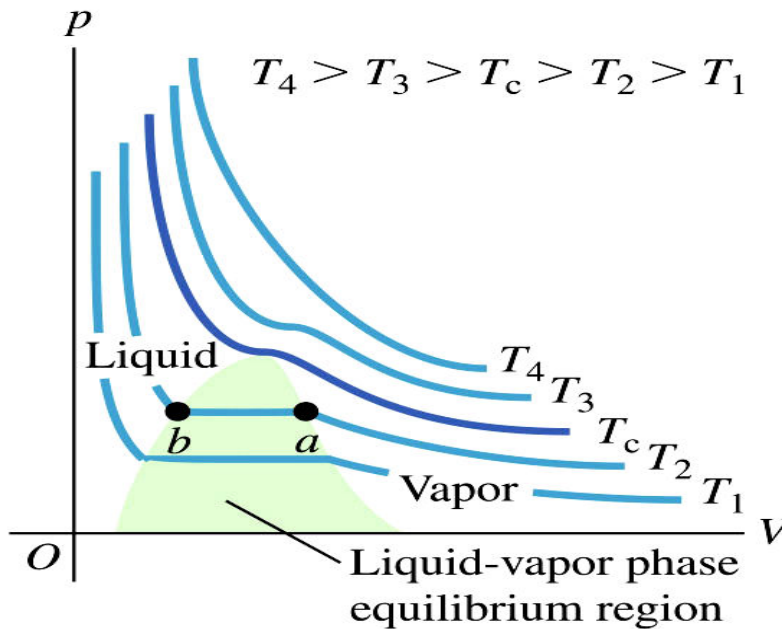
$b = \text{volume/mole}$ $a = \text{attraction_term}$

The volume available to the gas is reduced by nb and the pressure reduced due to intermolecular attractive forces.

For dilute ideal gases, the ration n/V is small and the ideal gas equation results.

The constants $a \ \& \ b$ are empirical.

Non-ideal gas behavior can be graphed as a gas approaches condensation by examining isotherms on P-V diagrams:

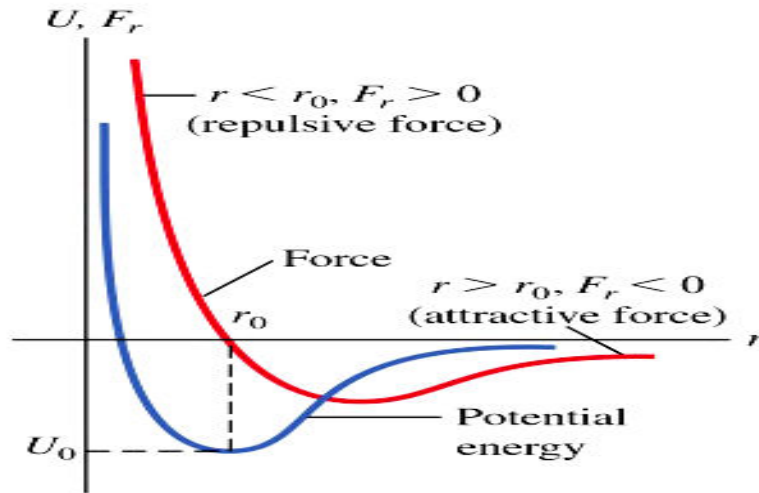


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Deviation from the expected V^{-1} along isotherms is due to intermolecular interaction.

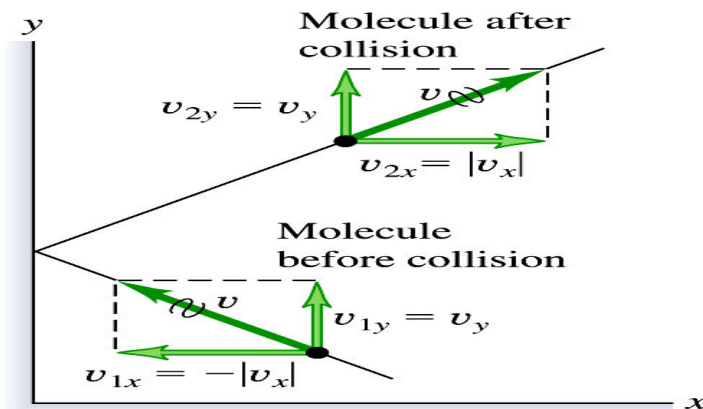
Molecular Interactions

Plotting potential energy and interaction force between two molecules of matter shows the effects of screening on molecules separated by distances on the order of atomic dimensions and the longer-range attractive van der Waals force between molecules



Kinetic Theory of Gases

Taking gas molecules as randomly interacting identical molecules undergoing elastic collisions with each other and the container walls, derive the ideal gas equation of state:



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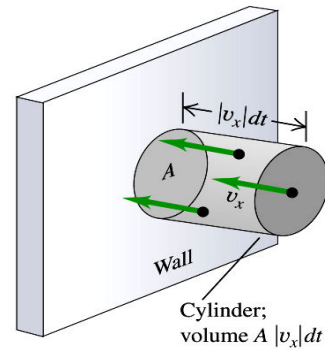
In a cubical container, each wall imparts a momentum change in the colliding molecule:

$$\Delta P_x = 2mv_x$$

$$F = \frac{\Delta P}{\Delta t} = \frac{2mv_x}{\Delta t}$$

The force at the wall is then:

$$\# \text{ of } _ \text{Collisions} = \frac{1}{2} \frac{N}{V} A v_x dt$$



All molecules assumed to have same magnitude $|v_x|$ of x-velocity

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$\Delta t = 2d / v_x$ Gives the correct force on the wall in Newton's 2nd Law:

$$F = \frac{2mv_x}{\Delta t} = \frac{mv_x^2}{d} \quad \text{Per Molecule.}$$

For N molecules,
$$F = \frac{m}{d} [v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2]$$

Taking the average v_x^2 for the x-coordinate square velocities:

$$\overline{v_x^2} = \frac{v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2}{N}$$

$$v^2 = v_x^2 + v_y^2 + v_z^2 = 3v_x^2 \quad \text{Motion in x, y, and z is identical.}$$

$$F = \frac{Nm\overline{v_x^2}}{d} = \frac{Nm}{d} \frac{\overline{v^2}}{3}$$

Pressure in the cube is:
$$P = \frac{F}{A} = \frac{Nm\overline{v^2}}{3dA} = \frac{1}{3} \frac{N}{V} m\overline{v^2}$$

This relates the macroscopic pressure to microscopic molecular square velocity.

$$PV = \frac{2}{3} N \frac{1}{2} m\overline{v^2}$$

From equipartition, each molecular degree of freedom yields $\frac{1}{2}kT$ of energy.

Therefore, with 3 translation degrees of freedom $\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$ and the gas temperature T is found to be directly related to kinetic activity as inferred earlier.

$$PV = NkT$$

RMS Velocity and Internal Energy

From $\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$ The RMS [root-mean-square] velocity for a molecule is:

$$\overline{v^2} = 3kT * \frac{1}{m} \qquad v_{RMS} = \sqrt{\frac{3kT}{m}}$$

T is in Kelvin and m is the mass of the molecule in kilograms.

The **RMS velocity** is the speed that molecules with average kinetic energy will possess.

The **internal energy** of an ideal gas depends on the type of gas and its temperature:

For **monatomic gas** like H_1 only molecular translation is possible and therefore by

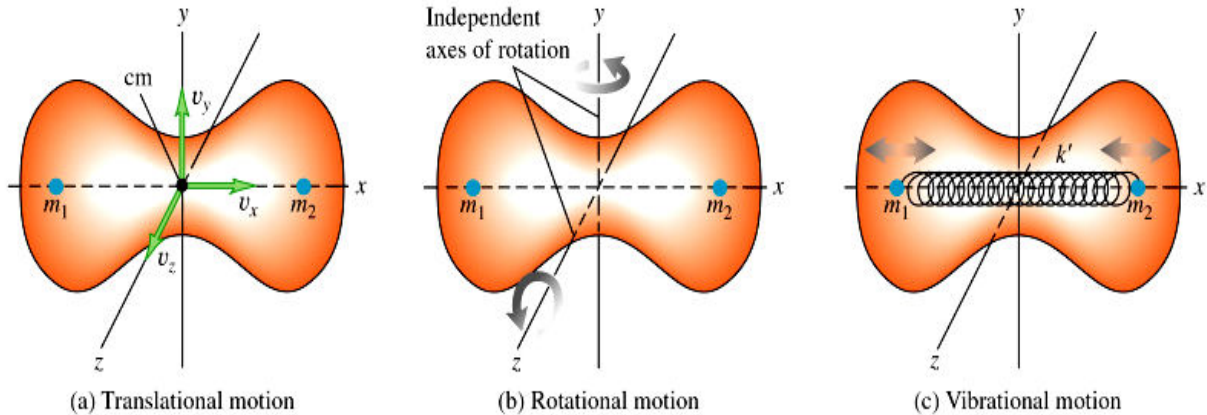
equipartition, $\frac{1}{2}kT$ for each translation degree of freedom $\rightarrow U = \frac{3}{2}kT$

For a **diatomic gas** like H_2 , there exist the possibility that at high temperatures, rotational degrees of freedom in the gas molecules excite. Two rotation degrees of freedom plus the

three degrees of translation freedom gives: $U = \frac{5}{2}kT$

At even higher temperatures, a diatomic molecule can also be excited into vibration modes with additional degrees of freedom that contribute to the internal energy: 7 total degrees

of freedom gives: $U = \frac{7}{2}kT$



Each degree of freedom represents an independent way in which the molecule may store thermal energy as internal energy.

Mean Free Path

The average distance each molecule travels before colliding with another molecule is its mean free path λ

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 \frac{N}{V}} \quad \text{Where } d \text{ is the molecular diameter.}$$

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 p} \quad \text{Where ideal gas is assumed.}$$

For air at sea level, $\lambda \sim 0.1$ microns.

Distribution of Molecular Speeds

From $\frac{1}{2} m \overline{v^2} = \frac{3}{2} kT$ we can find the RMS [root-mean-square] velocity for a molecule within a monatomic gas at temperature T:

$$\overline{v^2} = 3kT * \frac{1}{m} \quad \rightarrow \quad v_{RMS} = \sqrt{\frac{3kT}{m}}$$

The RMS velocity is the speed that molecules with average kinetic energy possess.

Velocities additionally of interest in this gas at temperature T include:

$$v_{Avg} = \sqrt{\frac{8kT}{\pi m}} \quad \text{The average molecular speed}$$

$$v_{Most_Probable} = \sqrt{\frac{2kT}{m}} \quad \text{The most probable velocity.}$$

These may be derived from the **Maxwell Speed Distribution Law** which is a probability distribution function describing the relative probability of finding a molecule at a given velocity in a gas of given temperature.

$$P(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}$$

When multiplied by the velocity interval dv , the product is the fraction of molecules with velocities in this interval centered around v .

Since the sum of such fractions is unity,

$$\int_0^{\infty} P(v)dv = 1 \Rightarrow \text{frac} = \int_{v_1}^{v_2} P(v)dv \quad \text{As the fraction within } [V_1, V_2] \text{ interval}$$

Calculating **most probable, RMS, and average speeds**, we integrate or maximize **P(v)**

$$v_{Avg} = \int_0^{\infty} vP(v)dv = \int_0^{\infty} v 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}$$

$$v_{RMS} = \left\{ \int_0^{\infty} v^2 P(v)dv \right\}^{1/2} = \left\{ \int_0^{\infty} v^2 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} \right\}^{1/2}$$

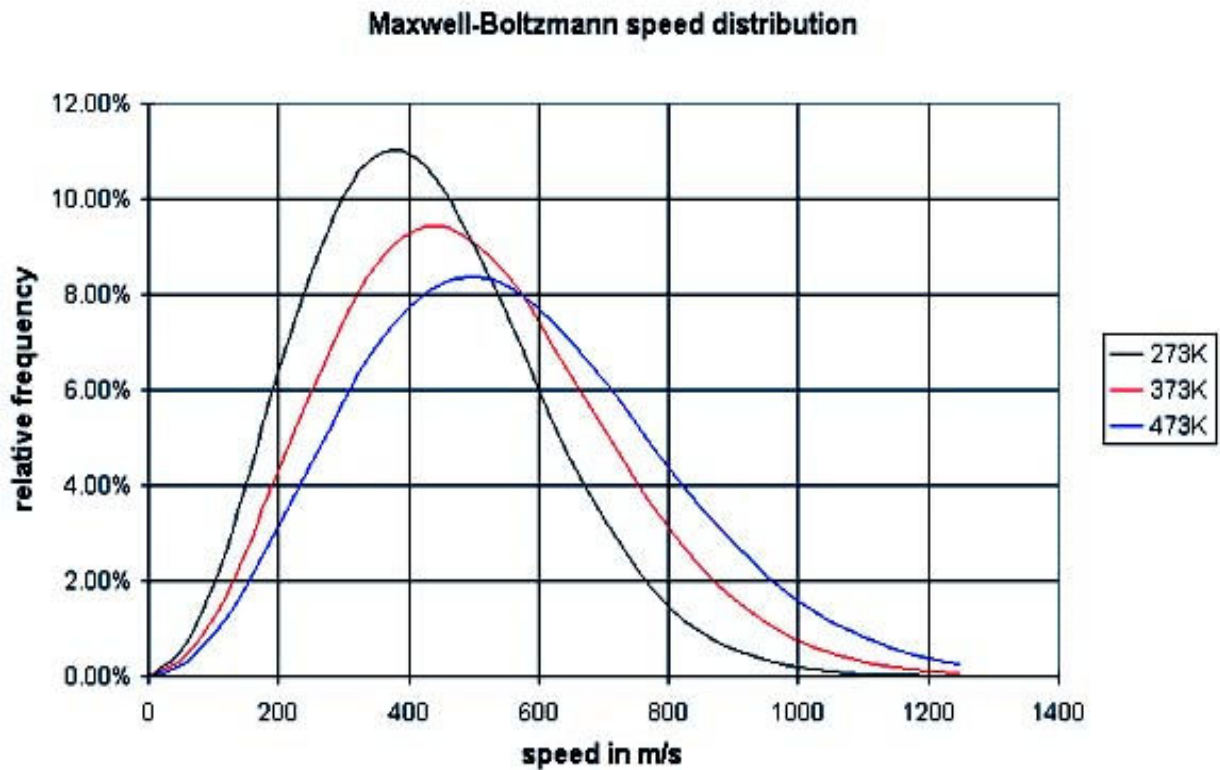
$$\frac{dP(v)}{dv} = 0 \Rightarrow v_{Most_probable}$$

The above integrals may be evaluated for $a > 0$ as:

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}$$

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdot \dots \cdot (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$$

Maxwell-Boltzmann speed distributions for varying temperature look like:



The shape of the [Maxwell Speed Distribution Law](#) curves has implication for many physical processes where temperature is a driving factor. As temperatures are increased, distributions are skewed further right to include molecules in the distribution tail with greater frequency thereby altering reaction rates.

Heat Capacities of Gases

Solids and liquids subjected to a temperature gradient respond as follows:

$$C = \frac{Q}{m\Delta T} \quad \rightarrow \quad \Delta T = \frac{Q}{mC}$$

For gases, the ΔT resulting from adding / extracting heat depends on whether this exchange took place while maintaining constant pressure or constant volume.

That is, for gases, there are two specific heat quantities of interest:

At **constant volume**, $W = 0$ and the 1st Law $\rightarrow \Delta U = Q$

$$Q = nC_V \Delta T \quad C_V \text{ is the molar specific heat at constant volume.}$$

$$C_V = \frac{Q}{n\Delta T} = \frac{\Delta U}{n\Delta T} = \frac{\frac{3}{2}nR\Delta T}{n\Delta T} = \frac{3}{2}R$$

$$C_V = 12.5 \frac{J}{mol \cdot K} \quad \text{Ideal monatomic gas.}$$

$$\Delta U = nC_V \Delta T \quad \text{In General.}$$

At constant pressure, $W \neq 0$ & the 1st Law $\rightarrow \Delta U = Q - W$

$$Q = nC_P\Delta T$$

$$C_P = \frac{Q}{n\Delta T} = \frac{\Delta U + W}{n\Delta T} = \frac{\frac{3}{2}nR\Delta T + P\Delta V}{n\Delta T} = \frac{3}{2}R + R = \frac{5}{2}R$$

$$C_P = C_V + R$$

$$C_P = 20.8 \frac{J}{mol \cdot K}$$

Easier to effect temperature change in a gas by transferring Q at a constant volume.

$$\Delta U = nC_P\Delta T - P\Delta V \quad \text{Isobaric process}$$

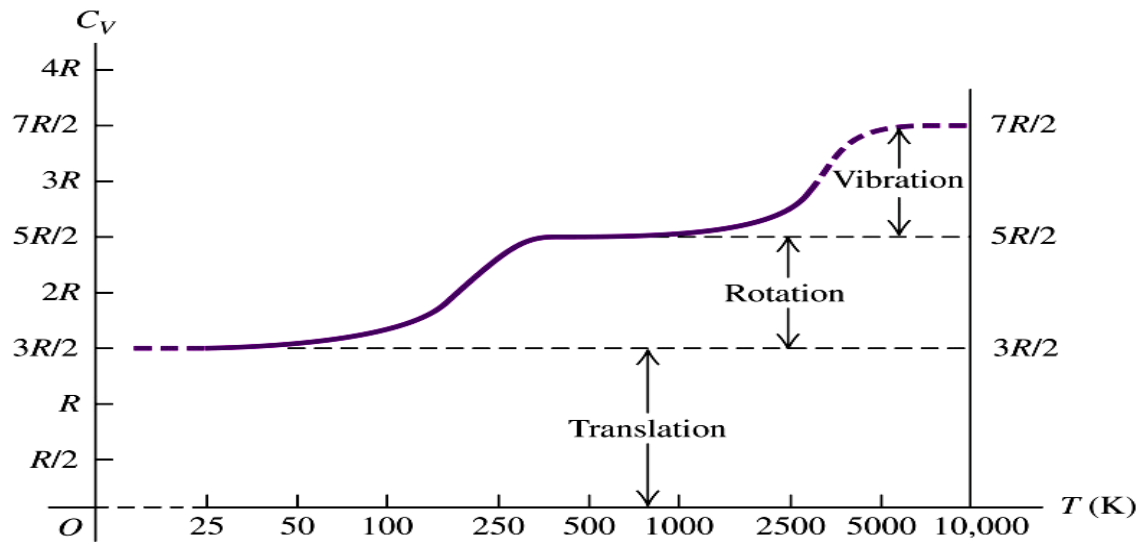
Further, since internal gas energy depends on degrees of molecular freedom we can evaluate C_V for different gas types at differing excitation levels:

$$C_V = \frac{\Delta U}{n\Delta T} = \frac{\frac{5}{2}nR\Delta T}{n\Delta T} = \frac{5}{2}R$$

Diatomic gas with 2 degrees of rotational freedom in addition to 3 translation dof.

$$C_V = \frac{\Delta U}{n\Delta T} = \frac{\frac{7}{2}nR\Delta T}{n\Delta T} = \frac{7}{2}R$$

Diatomic gas with 2 degrees of vibration freedom and 2 degrees of rotational freedom in addition to the 3 translation degrees of freedom.



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Solids

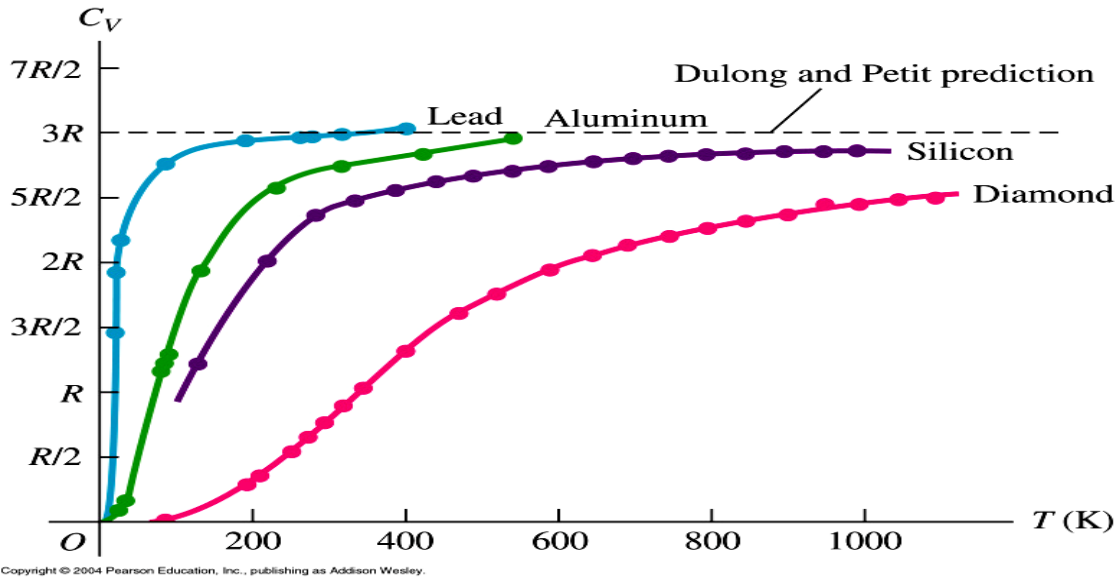
The molar heat capacity of solids approach an asymptotic value according to the **rule of Dulong and Petit:**

For a three-dimensional harmonic oscillator the average kinetic and potential energies are

equal $\frac{3}{2}kT$ such that the total mechanical energy is $E = 3NkT = 3nRT$

The molar specific heat therefore approaches a constant: $3R = 24.9 \frac{J}{mol \cdot K}$

As temperature is decreased the asymptotic value for molar specific heat of a solid decreases since the average energy available per molecule is less.



Approximate Specific Heats and Molar Heat Capacities (Constant Pressure)

| Substance | Specific Heat, c (J/kg · K) | M (kg/mol) | Molar Heat Capacity, C (J/mol · K) |
|-----------------------------|----------------------------------|-----------------|---|
| Aluminum | 910 | 0.0270 | 24.6 |
| Beryllium | 1970 | 0.00901 | 17.7 |
| Copper | 390 | 0.0635 | 24.8 |
| Ethanol | 2428 | 0.0461 | 111.9 |
| Ethylene glycol | 2386 | 0.0620 | 148.0 |
| Ice (near 0°C) | 2100 | 0.0180 | 37.8 |
| Iron | 470 | 0.0559 | 26.3 |
| Lead | 130 | 0.207 | 26.9 |
| Marble (CaCO ₃) | 879 | 0.100 | 87.9 |
| Mercury | 138 | 0.201 | 27.7 |
| Salt (NaCl) | 879 | 0.0585 | 51.4 |
| Silver | 234 | 0.108 | 25.3 |
| Water (liquid) | 4190 | 0.0180 | 75.4 |

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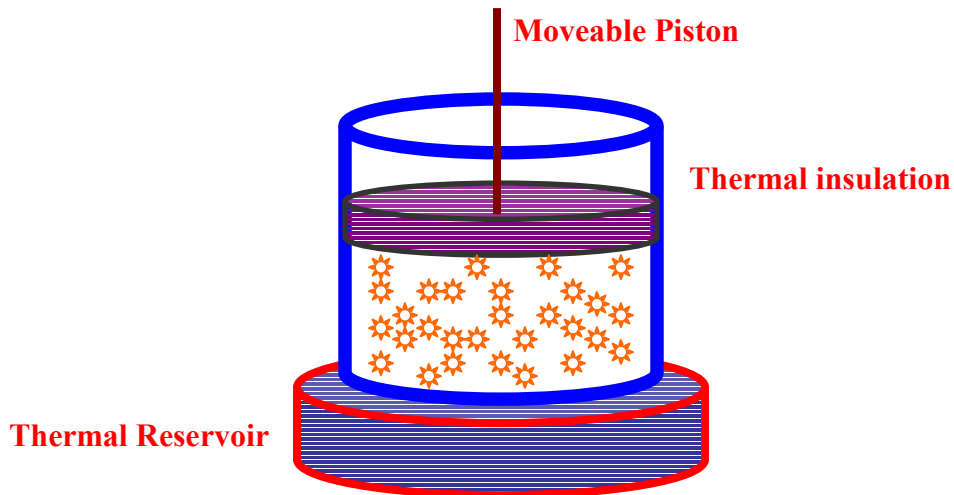
Note the approximate constant value near the predicted value $3R = 24.9 \frac{J}{mol \cdot K}$ for solid molar heat capacities in the right hand column.

First Law of Thermodynamics

Consider a thermodynamic system consisting of a thermally insulated container of gas molecules that can absorb heat from or transfer heat into a thermal reservoir.

A piston with cross-sectional area A can either do work on the system or extract work from the system.

The gas has intrinsic parameters $\{P, T, V, N\}$



Systems evolve from initial equilibrium $\{P, T, V, N \text{ specified}\}$ to a final equilibrium configuration with $\{P, T, V, N \text{ specified}\}$.

State functions depend only on intrinsic variables and changes in these functions depend on the starting point and ending point with path independence in between.

Internal energy is a state function, depending only on T

Heat and work are not state functions and therefore path dependent quantities.

The 'path' referred to is in P-V space, i.e., Pressure vs. Volume. The evolution of the system may be graphed P versus V.

To see why **work** is not a state function, consider the work done by the system during an expansion. For this evaluate the piston displacement:

$$W = \vec{F} \bullet \vec{d} = F \frac{A}{A} d = PV \quad \text{Isobaric (constant pressure) process.}$$

In general,

$$W = \int_{V_i}^{V_f} P dV \quad \rightarrow \quad \text{Work is the area underneath the P-V curve.}$$

$$W = \int_{V_i}^{V_f} \frac{NkT}{V} dV = NkT \ln \frac{V_f}{V_i} \quad \text{Ideal gas, for an Isothermal process}$$

Since this area depends on the path taken, work is path dependent.

Work, internal energy, and heat are related by the 1st Law of Thermodynamics:

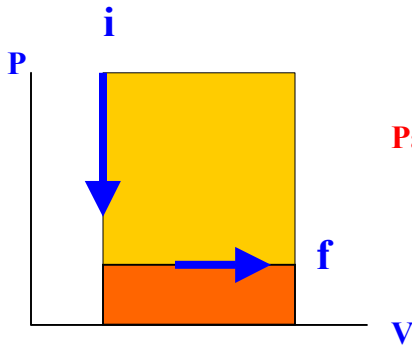
$$dU = dQ - dW$$

$$U = Q - W \quad \{W \text{ is work done by the system}\}$$

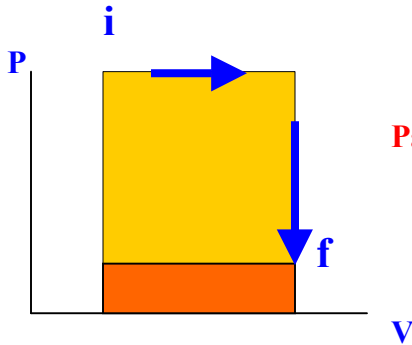
Then since internal energy is a state function heat must also be path dependent.

Path dependence and P-V diagrams

An example shows the path dependence of W:



Path 1 here gives W as the orange area $P\Delta V = \text{Joules}$



Path 2 gives W as the orange+gold areas $P\Delta V = \text{Joules}$

- 1) Q positive \rightarrow System absorbs energy; Q negative \rightarrow System gives off energy
- 2) W is positive for expansions against external force; W is negative for $V_f < V_i$
- 3) U increases with increasing T and U decreases as temperature is reduced.

Special Cases of the 1st Law of Thermodynamics

Adiabatic Process: Transition from initial to final states take place either very rapidly or in a well insulated system such that $Q = 0$, No heat is exchanged.

The 1st Law \rightarrow
$$\Delta U = -W$$

If the system does work, $W > 0 \rightarrow$ decreasing U

If work is done on the system, $W < 0 \rightarrow$ increasing U

In **throttling** a gas confined in a container under pressure undergoes a **free expansion** into an evacuated container by route of a small orifice.

In aerosol throttling, liquid expands passing through a small orifice and vaporizes into a gas. The phase change requires heat and since the process is adiabatic, this heat comes from the liquid reducing its temperature. The can cools.

Isochoric or Isovolumetric Process: Volume is held constant such that $\underline{W = P\Delta V = 0}$.

The 1st Law $\rightarrow \Delta U = Q$

All changes in U are due to heat input or extracted from the system.

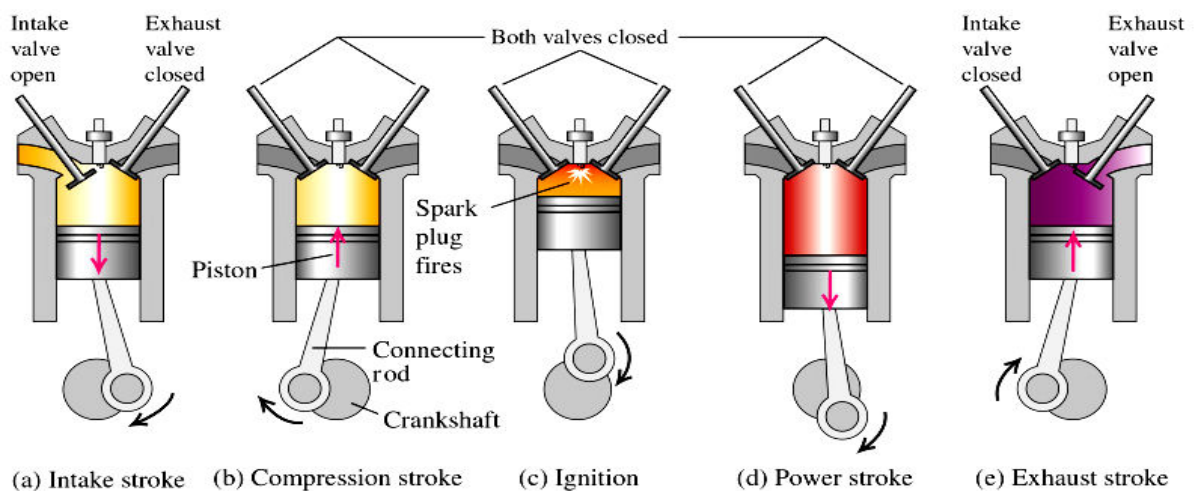
Sealed beverages in a refrigerator are cooled isochorically as heat is extracted.

Cyclic Processes A cyclic process is represented by a closed loop in P-V space. As the system evolves through the cycle $\Delta U = 0$.

The 1st Law $\rightarrow W = Q$

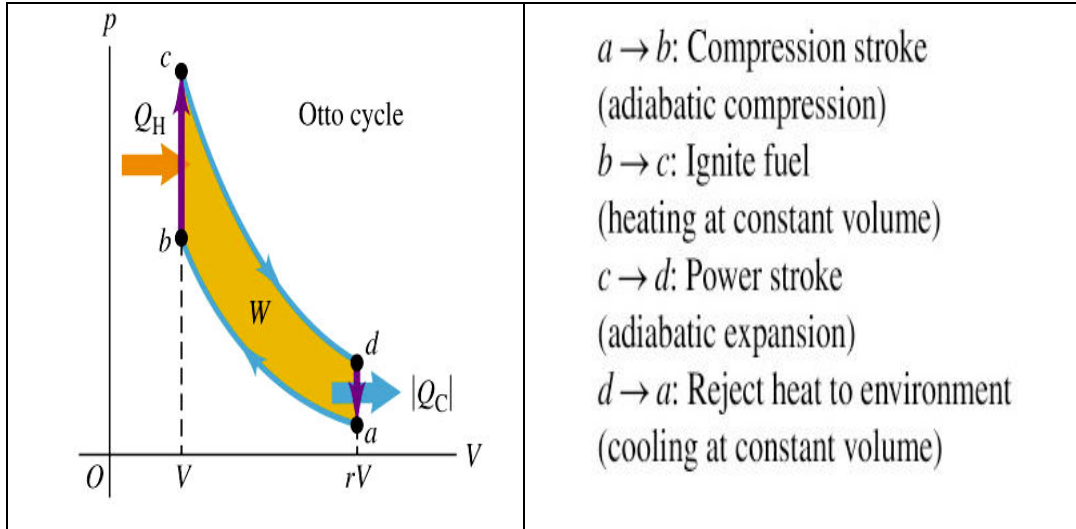
Cyclic processes are of general importance in **heat engines** that take a working substance, like gasoline/air, through a closed series of thermodynamic steps to extract work output from heat input.

- 1) **Intake of fuel and air**
- 2) **Compression of the mixture**
- 3) **Ignition by spark causing expansion and work done**
- 4) **Exhaust of combustion products.**



The compression stroke and power strokes are approximately adiabatic.

A **pV diagram** of the four-stroke process is the **Otto Cycle**:

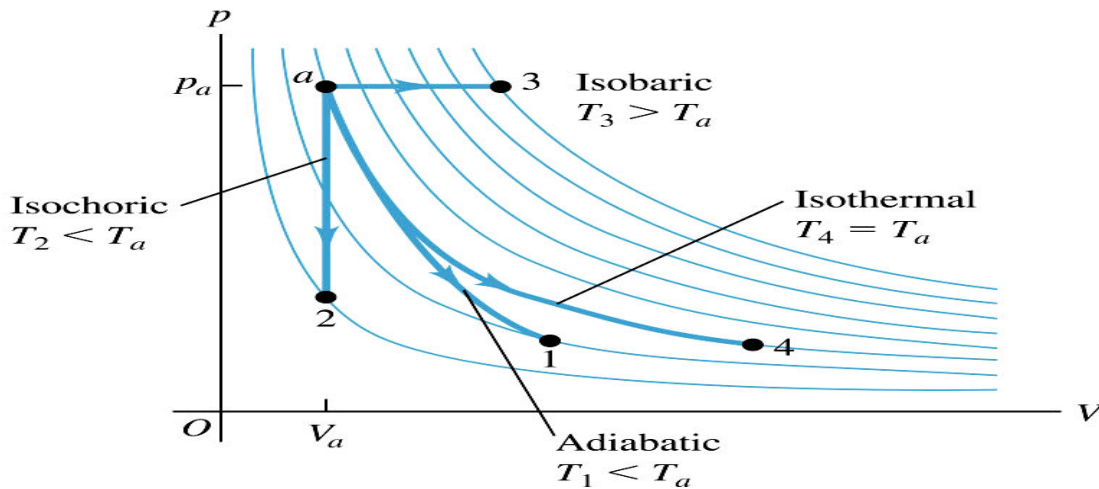


Free Expansion: Gas expanding adiabatically into a vacuum does no work since there isn't any pressure resisting the expansion. Since the process is adiabatic, heat exchange is also zero.

The 1st Law →
$$Q = W = \Delta U = 0$$

Thermodynamic Processes

Thermodynamic processes of interest currently are summarized in the figure below.



Note the difference between an adiabatic curve and an isothermal curve.

Adiabatic Expansion of an Ideal Gas

Adiabatic processes either takes place in a well-insulated enclosure or at such a fast rate that in either case, zero heat is exchanged with the environment.

From the 1st Law, taking $P \sim$ constant and ΔV small,

$$dU = -PdV \rightarrow$$

$$nC_V dT = -PdV \quad \text{Equation 1}$$

From the Ideal Gas Equation of State **PV = nRT**

$$PdV + VdP = nRdT$$

$$PdV + VdP = n\{C_P - C_V\}dT \quad \text{Equation 2}$$

Equating **n dT** from **1 & 2**

$$\frac{-PdV}{C_V} = \frac{PdV + VdP}{C_P - C_V}$$

Multiplying both by **1/VP**

$$\frac{-\frac{dV}{V}}{C_V} = \frac{\frac{dV}{V} + \frac{dP}{P}}{C_P - C_V}$$

$$\frac{\frac{dV}{V}}{C_P - C_V} - \frac{\frac{dV}{V}}{C_V} = \frac{\frac{dP}{P}}{C_P - C_V}$$

$$\frac{dP}{P} + \frac{C_P}{C_V} \frac{dV}{V} = 0$$

Integrating $\ln(P) + \gamma \ln(V) = \text{Const.}$

$$PV^\gamma = \text{Const} \quad \gamma = \frac{C_P}{C_V} = \frac{5}{3} \text{ Ideal monatomic gas.}$$

$$TV^{\gamma-1} = \text{Const}$$

An adiabatic process **not** governed by these relations is that of a **Free Expansion**.

The process has **Q = 0, W = 0 → ΔU = 0.**

ΔU = 0 → isothermal and the product **PV** is a constant not PV^γ

| Process | Constant Quantity | Relation Between Parameters |
|------------|---|--|
| Isobaric | Pressure | $Q = nC_p\Delta T$ And $W = P\Delta V$ |
| Isothermal | Temperature | $Q = W = nRT \ln \left\{ \frac{V_f}{V_i} \right\}$ And $\Delta U = 0$ |
| Isochoric | Volume | $Q = \Delta U = nC_v\Delta T$ And $W = 0$ |
| Adiabatic | PV^γ And / Or $TV^{\gamma-1}$ | $Q = 0$ And $\Delta U = -W$ |
