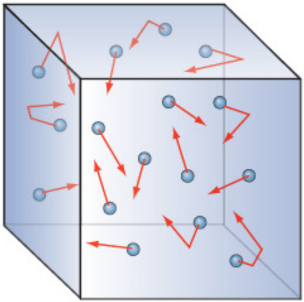
Chapter 3 - First Law of Thermodynamics



The ideal gas law is a combination of three intuitive relationships between pressure, volume, temp and moles.

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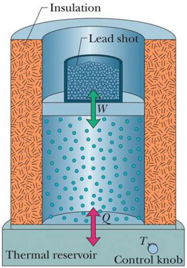
Penn State Hazleton
Fall 2013

First Law of Thermo

When a gas expands, it does work on its surroundings equal to

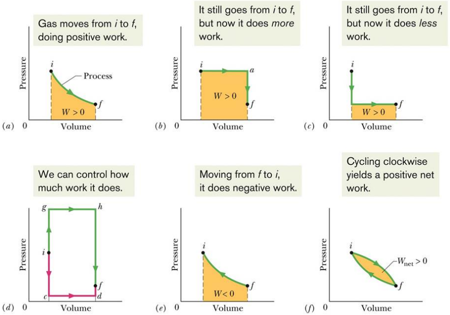
$$W = \int \vec{F}\cdot d\vec{s} = \int (pA)(ds) = \int p(A\,ds)$$

$$W = \int_{V_i}^{V_f} p\,dV$$



First Law of Thermo

We can graph p vs. volume—the area under the curve is work done.



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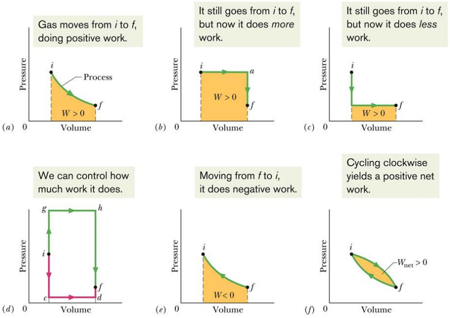

Use an inflated balloon to visualize the process.

First Law of Thermo

The thermodynamic quantities heat and work alter the energy of a system according to the first law of thermodynamics:

$$\Delta E_{int} = Q - W \quad (1)$$

$$dE_{int} = dQ - dW \quad (2)$$

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Heat increases the internal energy of the system, but work decreases the internal energy of the system.

First Law of Thermo

There are four very important cases involving the first law of thermodynamics.

Table 18-5 The First Law of Thermodynamics: Four Special Cases

The Law: $\Delta E_{\text{int}} = Q - W$ (Eq. 18-26)

Process	Restriction	Consequence
Adiabatic	$Q = 0$	$\Delta E_{\text{int}} = -W$
Constant volume	$W = 0$	$\Delta E_{\text{int}} = Q$
Closed cycle	$\Delta E_{\text{int}} = 0$	$Q = W$
Free expansion	$Q = W = 0$	$\Delta E_{\text{int}} = 0$

First Law of Thermo

Which one of the following statements is not consistent with the first law of thermodynamics?

(a) The internal energy of a finite system must be finite.

(b) An engine may be constructed such that the work done by the machine exceeds the energy input to the engine.

(c) An isolated system that is thermally insulated cannot do work on its surroundings nor can work be done on the system.

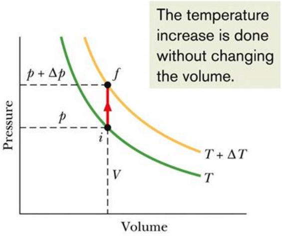
(d) The internal energy of a system decreases when it does work on its surroundings and there is no flow of heat.

(e) An engine may be constructed that gains energy while heat is transferred to it and work is done on it.

Molar Specific Heat

When heat is added to a gas at constant volume, its temperature changes according to

$$Q = nC_V \Delta T \qquad (3)$$



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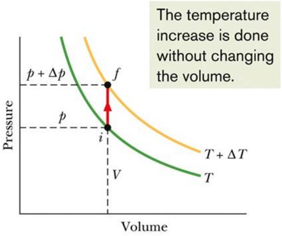

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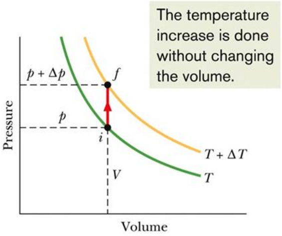

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$$C_V = \frac{\Delta E_{int}}{n\Delta T} = \frac{\frac{3}{2}nRT}{n\Delta T} = \frac{3}{2}R \tag{4}$$

Molar Specific Heat

When heat is added to a gas at constant pressure, its temperature again changes according to

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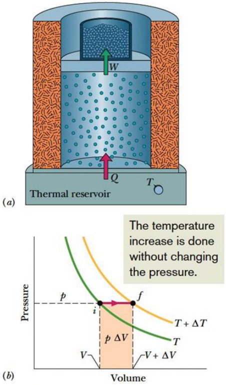

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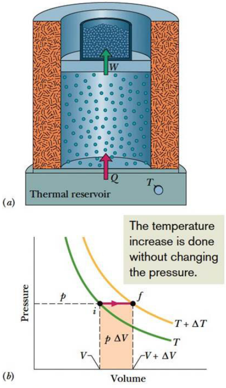

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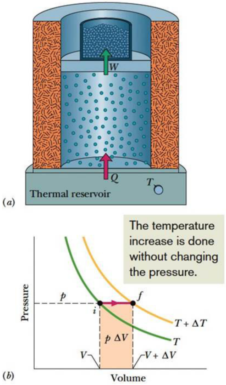

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$$\Delta E_{int} = nC_V\Delta T = Q - W$$

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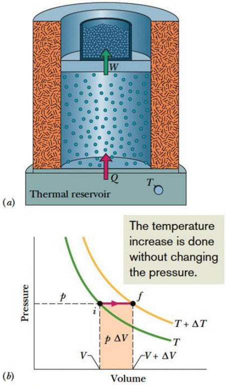

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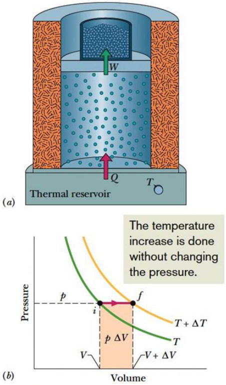

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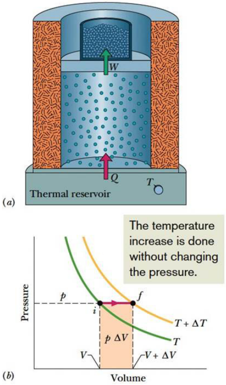

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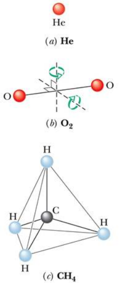
$$\begin{aligned} \Delta E_{int} &= nC_V\Delta T = Q - W \\ nC_V\Delta T &= nC_p\Delta T - nR\Delta T \\ C_V &= C_p - R \\ C_p &= C_V + R \end{aligned}$$

Molar Specific Heat

Molecules can store energy based upon their geometries, altering their specific heats.

Table 19-3 Degrees of Freedom for Various Molecules

Molecule	Example	Degrees of Freedom: Translational	Rotational	Total (f)	Predicted Molar Specific Heats: C_V (Eq. 19-51)	$C_p = C_V + R$
Monatomic	He	3	0	3	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic	O_2	3	2	5	$\frac{5}{2}R$	$\frac{7}{2}R$
Polyatomic	CH_4	3	3	6	$3R$	$4R$



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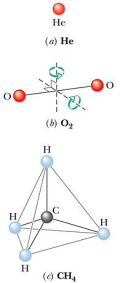
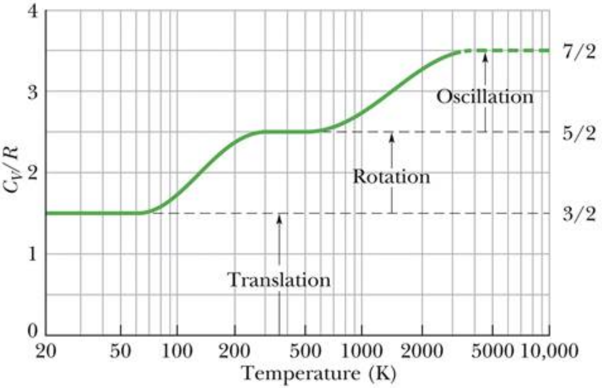


Each degree of freedom gets about

- $\frac{1}{2}kT$ energy per molecule
- $\frac{1}{2}RT$ energy per mole

Molar Specific Heat

Molecules can also store vibrational energy, but only at higher temperatures.



Molar Specific Heat

A monatomic gas particle has only 3 degrees of freedom and each particle in the gas has a thermal energy equal to $(3/2)kT$. How many degrees of freedom does a diatomic gas particle have and how much thermal energy does each molecule have?

(a) 2, kT

(b) 3, $(3/2)kT$

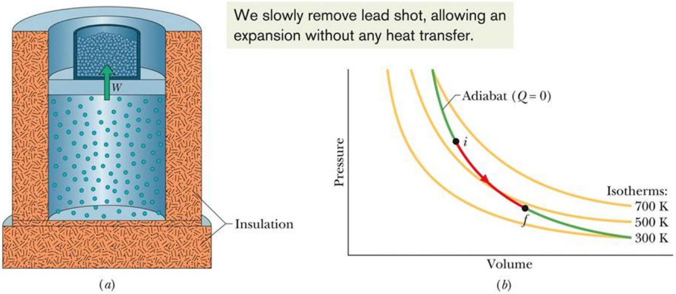
(c) 4, $2kT$

(d) 5, $(5/2)kT$

(e) 6, $3kT$

Adiabatic Expansion

Adiabatic expansion means that the volume changes while $Q = 0$; i.e., no heat is transferred.



Let's derive the curve in (b) from first principles!

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Taking partials of the ideal gas law and using $C_p = C_V + R$,

$$p\,dV + V\,dp = nR\,dT$$

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Adiabatic Expansion

Integrating this equation, we find

$$\ln p + \frac{C_p}{C_V} \ln V \quad = \quad \text{constant}$$

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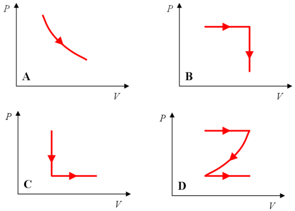
This also implies (using ideal gas law):

$$\begin{aligned} p_i V_i^{\gamma} &= p_f V_f^{\gamma} \\ T_i V_i^{\gamma-1} &= T_f V_f^{\gamma-1} \end{aligned}$$

Adiabatic Expansion

Consider the following pressure-volume graphs. Which of these graphs represents the behavior of a gas undergoing free expansion?



E. None of the graphs represent a gas undergoing free expansion.