Molar Specific Heats of Other Materials

- The internal energy of more complex gases must include contributions from the rotational and vibrational motions of the molecules
- In the cases of solids and liquids heated at constant pressure, very little work is done since the thermal expansion is small and C_P and C_V are approximately equal

A Microscopic Description of Temperature

- Simplifying the equation relating temperature and kinetic energy gives

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_{\mathrm{B}}T$$

- This can be applied to each direction,

$$\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}k_{\mathrm{B}}T$$

with similar expressions for v_y and v_z

A Microscopic Description of Temperature

- Each translational degree of freedom contributes an equal amount to the energy of the gas
  - In general, a degree of freedom refers to an independent means by which a molecule can possess energy
- A generalization of this result is called the **theorem of equipartition of energy**

Theorem of Equipartition of Energy

- Each degree of freedom contributes $1/2k_BT$ to the energy of a system, where possible degrees of freedom in addition to those associated with **translation** arise from **rotation** and **vibration** of molecules

The total number of “types of motion” per molecule consisting of n atoms is equal **3n**

Total Kinetic Energy

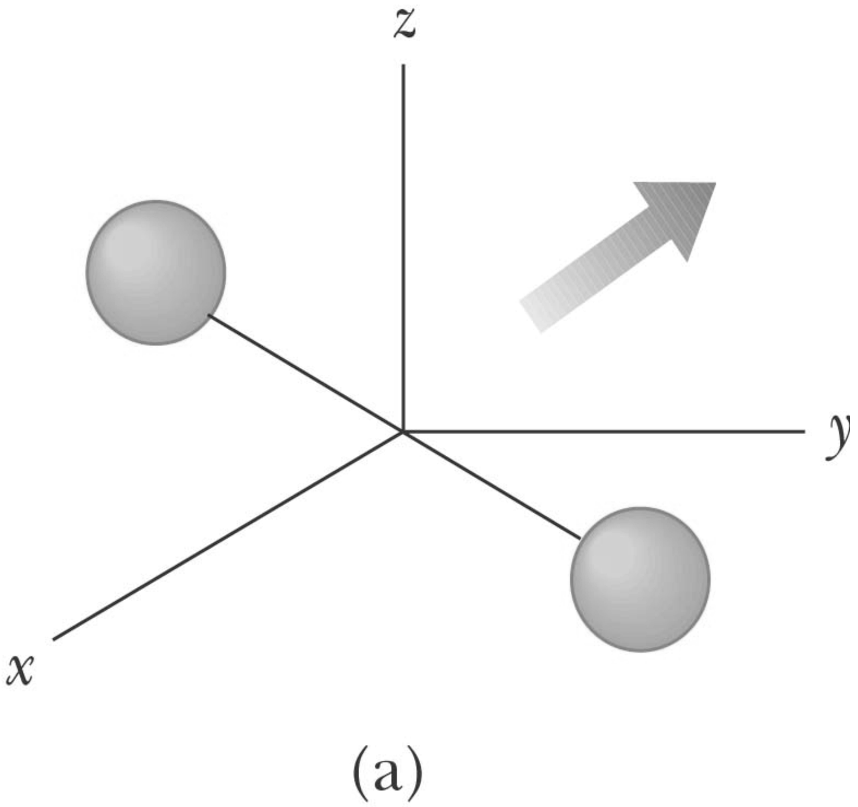
- The total kinetic energy is just *N* times the kinetic energy of each molecule

$$K_{\text{tot trans}} = N\left(\frac{1}{2}m\overline{v^2}\right) = \frac{3}{2}Nk_{\text{B}}T = \frac{3}{2}nRT$$

- If we have a gas with only translational energy, this is the internal energy of the gas
- This tells us that the internal energy of an ideal gas depends only on the temperature

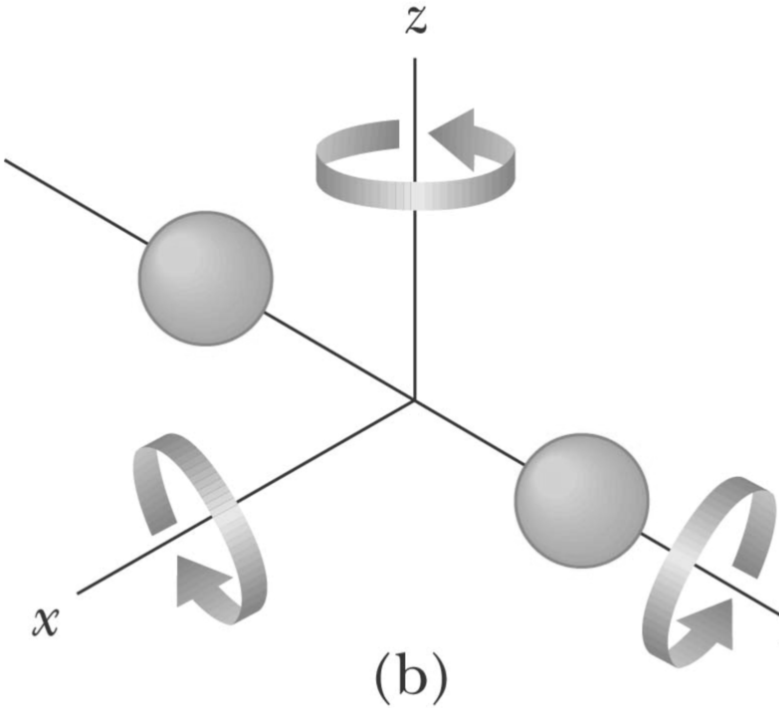
Equipartition of Energy

- With complex molecules, other contributions to internal energy must be taken into account
- One possible energy is the translational motion of the center of mass



Equipartition of Energy

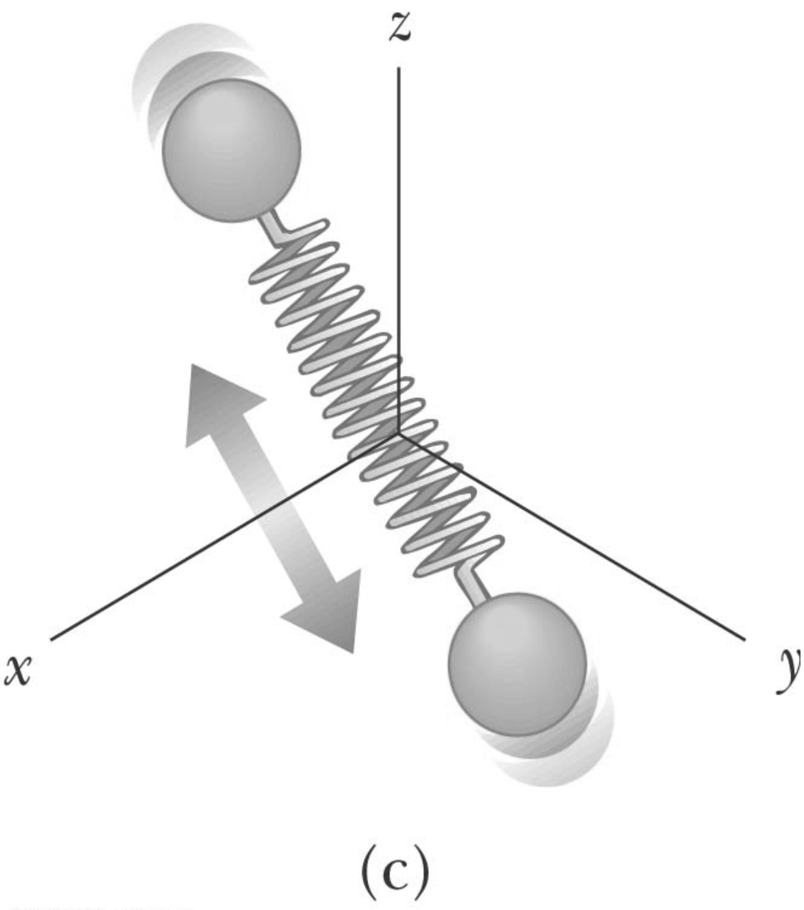
- Rotational motion about each of the various axes **contributes 1/2$k_B T$ to the energy of a system**
  - We can neglect the rotation around the *y* axis since it is negligible compared to the *x* and *z* axes



Equipartition of Energy

- The molecule can also vibrate
- There is **kinetic energy** and **potential energy** associated with the vibrations
- **Each of this is contributing 1/2$k_B T$**

  to the energy of a system, so total per one vibration is $k_B T$



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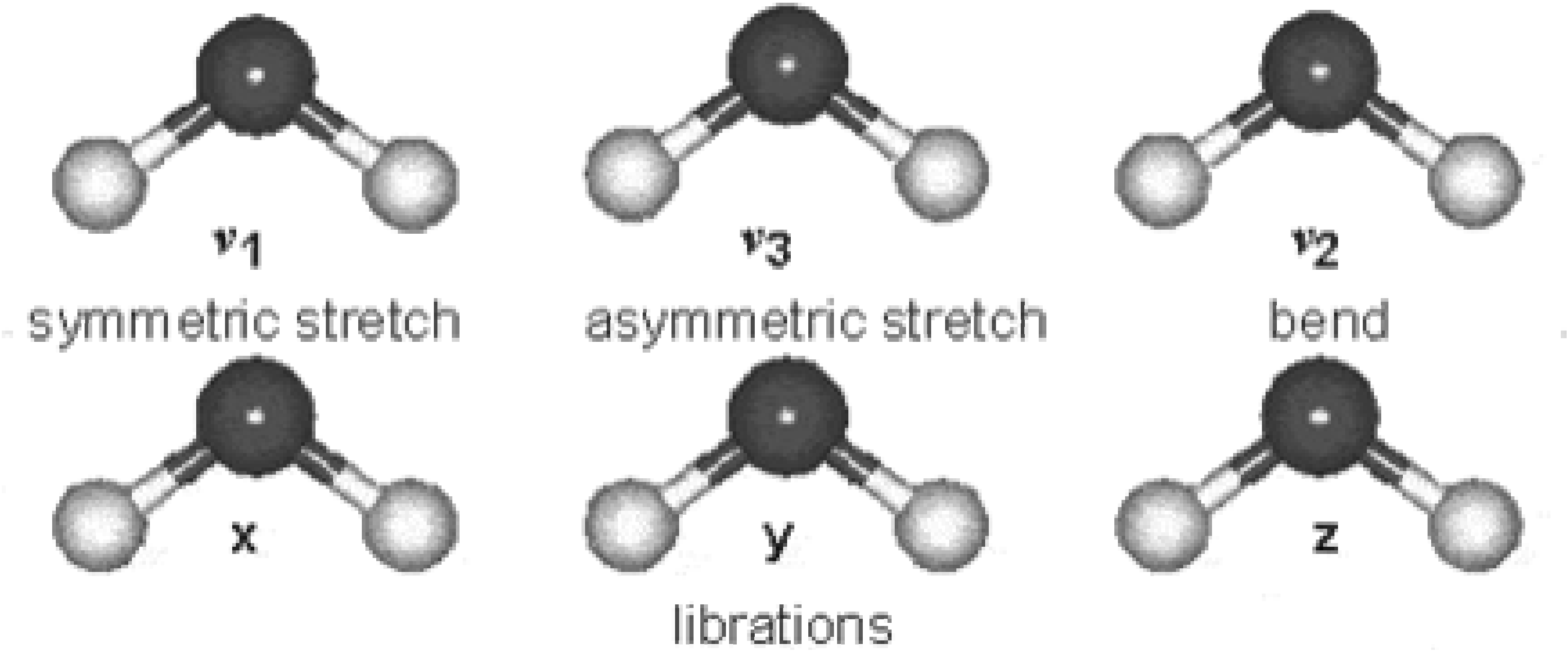
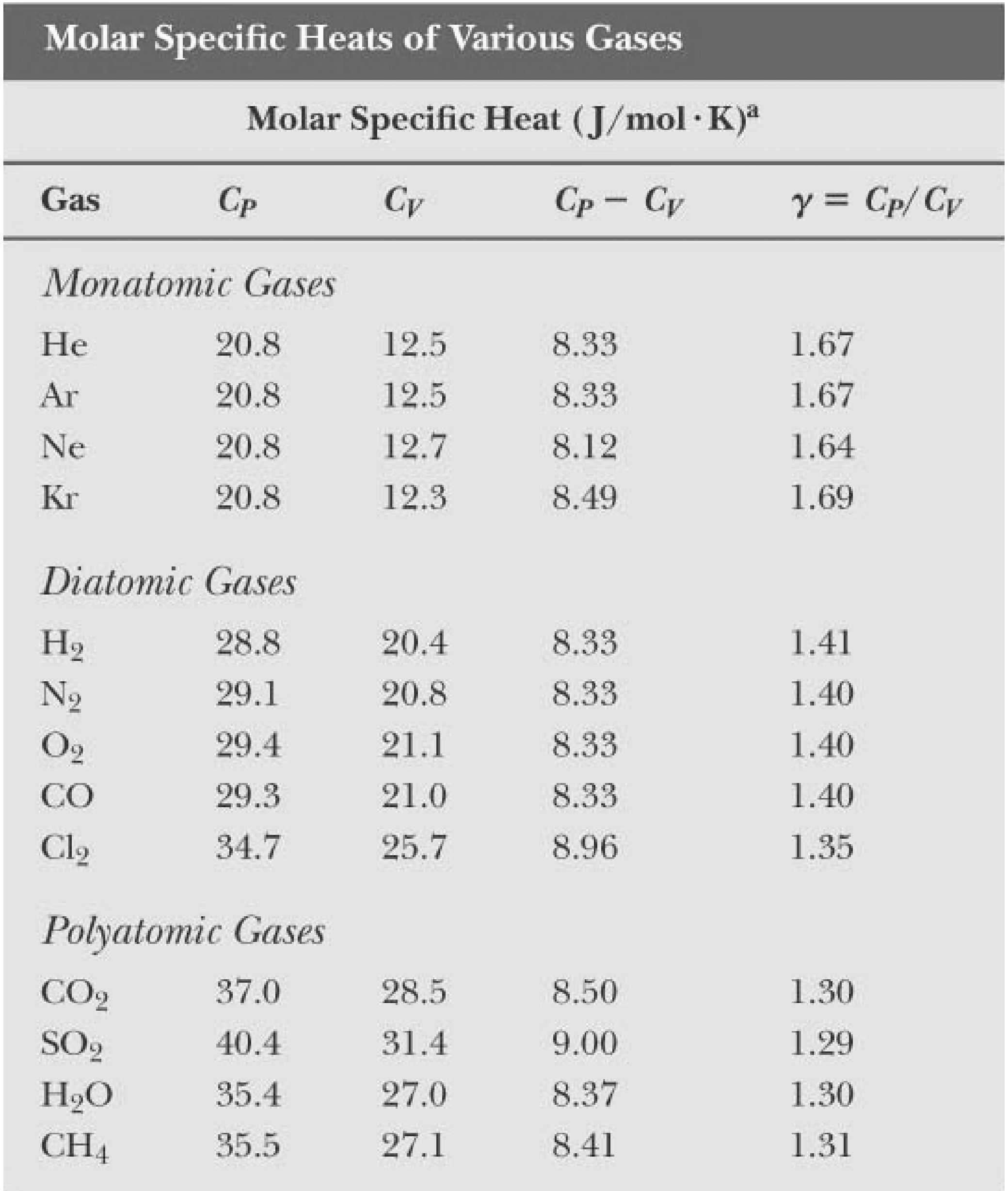
Water vibrations and rotations



http://www.lsbu.ac.uk/water/vibrat.html

Values of Molar Specific Heats



Molar Specific Heats of Various Gases

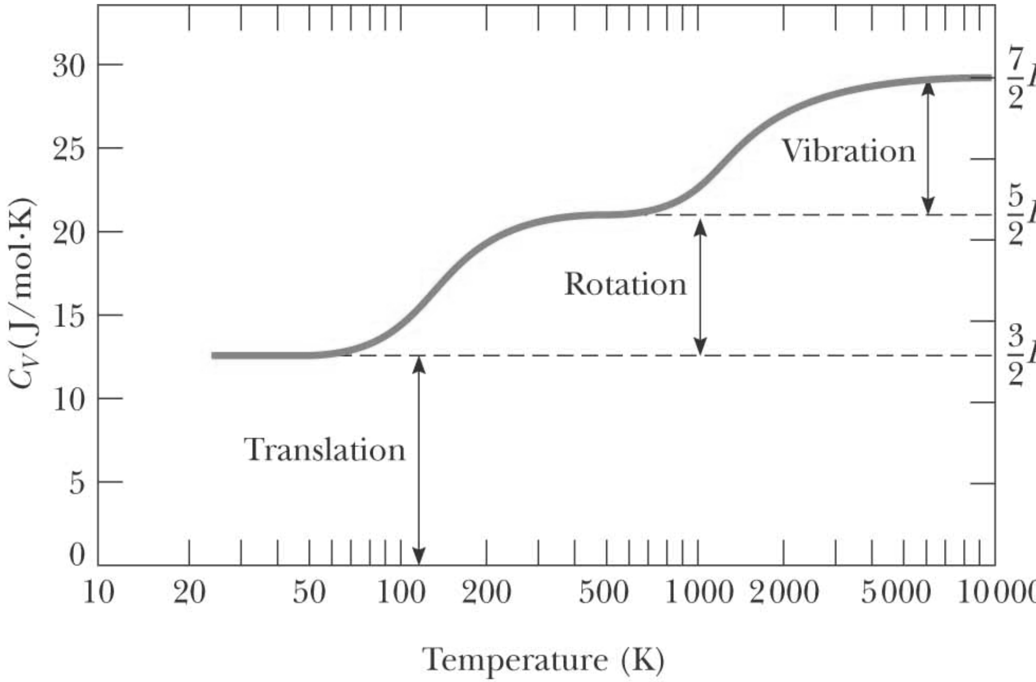
	Molar Specific Heat (J/mol·K)[a]			
Gas	C_P	C_V	$C_P - C_V$	$\gamma = C_P/C_V$
Monatomic Gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
Diatomic Gases				
H_2	28.8	20.4	8.33	1.41
N_2	29.1	20.8	8.33	1.40
O_2	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl_2	34.7	25.7	8.96	1.35
Polyatomic Gases				
CO_2	37.0	28.5	8.50	1.30
SO_2	40.4	31.4	9.00	1.29
H_2O	35.4	27.0	8.37	1.30
CH_4	35.5	27.1	8.41	1.31

Equipartition of Energy: Diatomic molecule

- The **translational** motion adds **three** degrees of freedom
- The **rotational** motion adds **two** degrees of freedom
- The **vibrational** motion adds **two** more degrees of freedom
- Therefore, $E_{\text{int}} = 7/2\ nRT$ and $C_V = 7/2\ R$

Agreement with Experiment

- Molar specific heat is a function of temperature
- At low temperatures, a diatomic gas acts like a monatomic gas
  - $C_V = 3/2\ R$



Agreement with Experiment: H_2

- At about room temperature, the value increases to $C_V = 5/2\ R$
  - This is consistent with adding rotational energy but not vibrational energy
- At high temperatures, the value increases to $C_V = 7/2$ R
  - This includes vibrational energy as well as rotational and translational

Complex Molecules

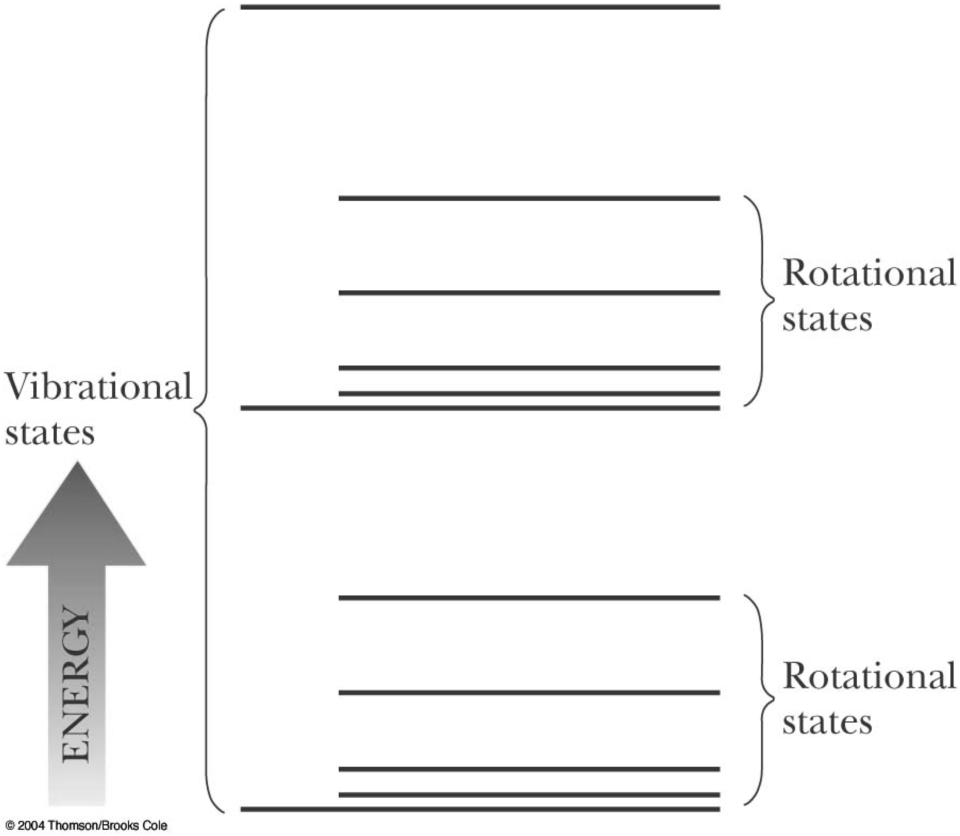
- For molecules with more than two atoms, the vibrations are more complex
- The number of degrees of freedom is larger
- The more degrees of freedom available to a molecule, the more “ways” there are to store energy
  - This results in a higher molar specific heat

Quantization of Energy

- To explain the results of the various molar specific heats, we must use some quantum mechanics
  - Classical mechanics is not sufficient
- In quantum mechanics, the energy is proportional to the frequency of the wave representing the frequency
- The energies of atoms and molecules are quantized

Quantization of Energy

- This energy level diagram shows the rotational and vibrational states of a diatomic molecule
- The lowest allowed state is the **ground state**



Quantization of Energy

- The vibrational states are separated by larger energy gaps than are rotational states
- At low temperatures, the energy gained during collisions is generally not enough to raise it to the first excited state of either rotation or vibration

Quantization of Energy

- Even though rotation and vibration are classically allowed, they do not occur
- As the temperature increases, the energy of the molecules increases
- In some collisions, the molecules have enough energy to excite to the first excited state
- As the temperature continues to increase, more molecules are in excited states

Quantization of Energy

- At about room temperature, rotational energy is contributing fully
- At about 1000 K, vibrational energy levels are reached
- At about 10 000 K, vibration is contributing fully to the internal energy

Molar Specific Heat of Solids

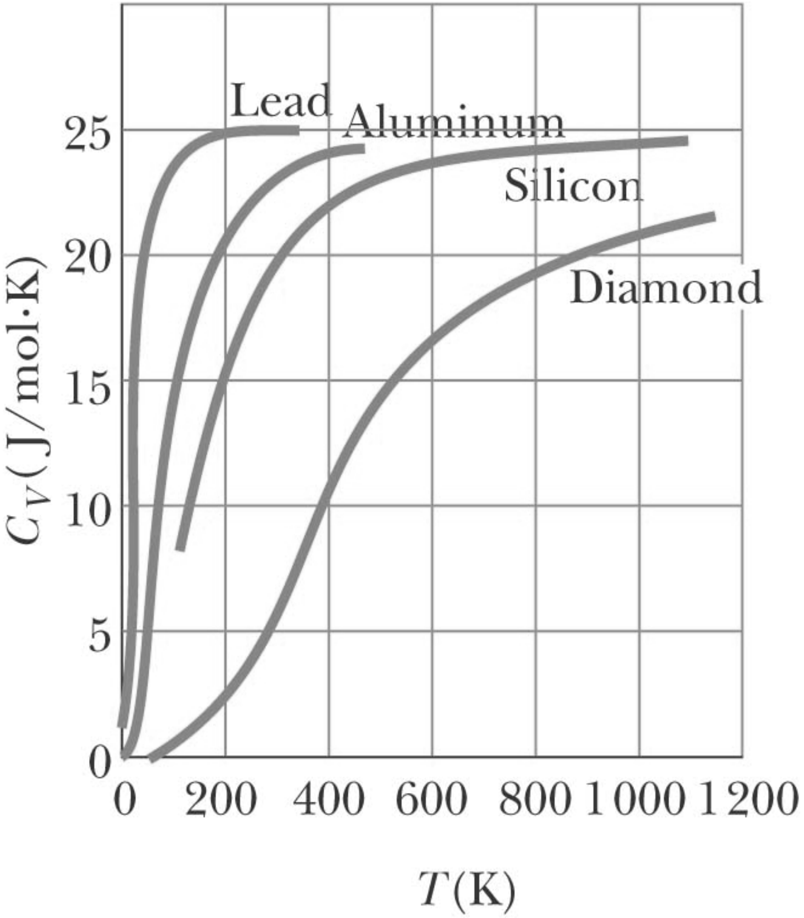
- Molar specific heats in solids also demonstrate a marked temperature dependence
- Solids have molar specific heats that generally decrease in a nonlinear manner with decreasing temperature
- It approaches zero as the temperature approaches absolute zero

DuLong-Petit Law

- At high temperatures, the molar specific heats approach the value of 3R
  - This occurs above 300 K
- The molar specific heat of a solid at high temperature can be explained by the equipartition theorem
  - Each atom of the solid has six degrees of freedom
  - The internal energy is 3 nRT and $C_v = 3\,R$

Molar Specific Heat of Solids, Graph

- As *T* approaches 0, the molar specific hea approaches 0
- At high temperatures, C_V becomes a constant at ~3*R*



Boltzmann Distribution Law

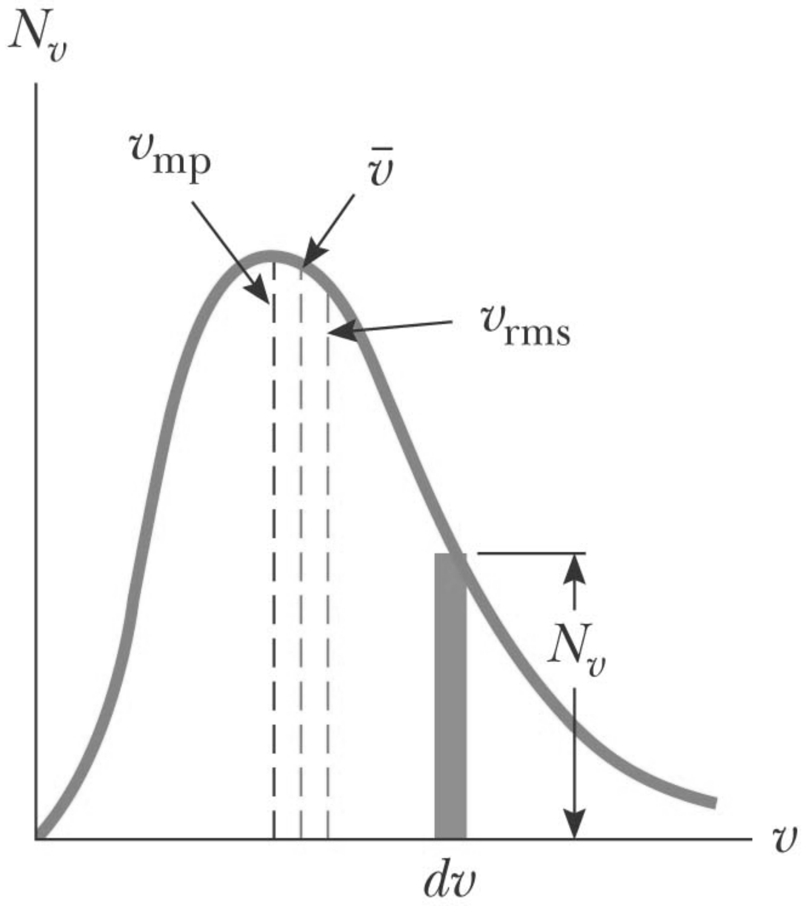
- The motion of molecules is extremely chaotic
- Any individual molecule is colliding with others at an enormous rate
  - Typically at a rate of a billion times per second
- We add the **number density** $n_V(E)$
  - This is called a distribution function
  - It is defined so that $n_V(E)\,dE$ is the number of molecules per unit volume with energy between E and $E + dE$

Number Density and Boltzmann Distribution Law

- From statistical mechanics, the number density is $n_V(E) = n_o e^{-E/k_B T}$
- This equation is known as the Boltzmann distribution law
- It states that the probability of finding the molecule in a particular energy state varies exponentially as the energy divided by $k_B T$

Distribution of Molecular Speeds

- The observed speed distribution of gas molecules in thermal equilibrium is shown at right
- N_V is called the **Maxwell-Boltzmann speed distribution function**



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