

Chapter 06

Equipartition of Energy

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Energetically accessible degrees of freedom

In kinetic theory of gases we consider translational motion of **monatomic gas** and learned that temperature is a measure of average translational kinetic energy,

$$pV = n\frac{2}{3}N_A\bar{\epsilon}_k = nRT \quad \text{or} \quad \bar{\epsilon}_k = \frac{3}{2}k_B T$$

What about a polyatomic gas where there is translational, rotational, and vibrational motion?

Definition

Equipartition of energy theorem says that energy is distributed, on average, equally among all energetically accessible degrees of freedom, such as those associated with molecular translations, molecular rotations, bond vibrations, and electronic motion.

More specifically, it says *there will be an average thermal energy of $\frac{1}{2}k_B T$ associated with each coordinate that shows up squared in the total energy expression.*

Monoatomic gas

Simplest model of monoatomic gas only considers translational motion.

Translational Energy

For each particle (atom) the energy is

$$E_{\text{trans}} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

3 independent coordinates, p_x , p_y , and p_z , appear squared. According to equipartition of energy theorem the average thermal energy of a monoatomic gas atom is

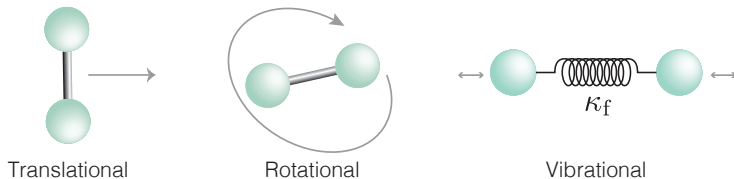
$$\bar{\epsilon}_{\text{trans}} = 3 \left(\frac{1}{2} k_B T \right) = \frac{3}{2} k_B T$$

or internal molar energy of

$$U_m = \frac{3}{2} RT \quad \text{monoatomic gas}$$

Diatomic gas molecules

- For diatomic gas molecule total energy expression will include same contribution for translational motion as monoatomic gas except coordinates are associated with center of mass of molecule.
- In addition to translation, energy expression for diatomic molecules will include additional contributions from internal motions such as rotational and vibrational motion.



Diatomic gas molecules

Rotational Energy

For a diatomic molecule rotational energy is

$$E_{\text{rot}} = \frac{1}{2}I_b\omega_b^2 + \frac{1}{2}I_c\omega_c^2$$

I_b and I_c are principal moments of inertia and ω_b and ω_c are components of angular velocity vector. Recall: diatomic molecule is linear so $I_a = 0$.

Vibrational Energy

For a diatomic molecule vibrational energy (modeled as harmonic oscillator) is

$$E_{\text{vib}} = \underbrace{\frac{p_r^2}{2m_r}}_{\text{Kinetic}} + \underbrace{\frac{1}{2}\kappa_f(r - r_e)^2}_{\text{Potential}}$$

Diatomic gas molecules

Applying the equipartition of energy theorem for a diatomic we count

3	for p_x^2, p_y^2, p_z^2	← translational
+2	for ω_b^2, ω_c^2	← rotational
+2	for p_r^2, r^2	← vibrational
<hr/>		
7		← total

Average thermal energy of gas atom is

$$\bar{\epsilon} = 7 \left(\frac{1}{2} k_B T \right) = \frac{7}{2} k_B T$$

For diatomic gas this predicts internal molar energy of

$$U_m = \frac{7}{2} RT \quad \text{diatomic gas}$$

Linear polyatomic gas molecules

For a polyatomic gas molecule containing X atoms we will consider two cases: linear and non-linear molecules. In the case of linear molecules we count

$$\begin{array}{rcl} 3 & \text{for } p_x^2, p_y^2, p_z^2 & \leftarrow \text{translational} \\ +2 & \text{for } \omega_b^2, \omega_c^2 & \leftarrow \text{rotational} \\ +2(3X - 5) & & \leftarrow \text{vibrational} \\ \hline 6X - 5 & & \leftarrow \text{total} \end{array}$$

Average thermal energy of linear polyatomic gas molecule is

$$\bar{\epsilon} = (6X - 5) \left(\frac{1}{2} k_B T \right)$$

For linear polyatomic gas molecule this predicts internal molar energy of

$$U_m = (6X - 5) \left(\frac{1}{2} RT \right), \quad \text{linear polyatomic gas}$$

Non-linear polyatomic gas molecules

In the case of non-linear molecule containing X atoms we count

$$\begin{array}{rcl} 3 & \text{for } p_x^2, p_y^2, p_z^2 & \leftarrow \text{translational} \\ +3 & \text{for } \omega_a^2, \omega_b^2, \omega_c^2 & \leftarrow \text{rotational} \\ +2(3X - 6) & & \leftarrow \text{vibrational} \\ \hline 6X - 6 & & \leftarrow \text{total} \end{array}$$

Average thermal energy of non-linear polyatomic gas molecule is

$$\bar{\epsilon} = (6X - 6) \left(\frac{1}{2} k_B T \right)$$

For non-linear polyatomic gas molecule this predicts internal molar energy of

$$U_m = 3(X - 1)RT, \quad \text{non-linear polyatomic gas}$$

Heat capacity of a gas

Heat capacity of a gas

Molar heat capacity at constant volume is given by

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T} \right)_V$$

How does equipartition theorem prediction do predicting heat capacities?

Heat capacity of a monoatomic gas

For monoatomic gas equipartition theorem predicts $U_m = \frac{3}{2}RT$.

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T} \right)_V = \frac{3}{2}R = 12.47 \text{ J}/(\text{mol}\cdot\text{K})$$

and experimental heat capacities for a few monoatomic gases are ...

Gas	$C_{V,m}$ (measured) / J/(mol·K)
He	12.47
Ne	12.47
Ar	12.47

Impressive agreement!!

Heat capacity of a diatomic gas

For diatomic gas the equipartition theorem predicts $U_m = \frac{7}{2}RT$

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T} \right)_V = \frac{7}{2}R = 29.10 \text{ J}/(\text{mol}\cdot\text{K})$$

Experimental heat capacities for a few diatomic gases are ...

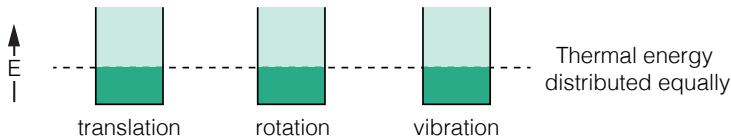
Gas	$C_{V,m}$ (measured) / J/(mol·K)
H ₂	20.50
N ₂	20.50
O ₂	21.50

Measured heat capacity is consistently lower than prediction by value close to $R \approx 8.31446 \text{ J}/(\text{mol}\cdot\text{K})$.

What went wrong?

Heat capacity of a gas

Equipartition theorem assumes thermal energy is distributed equally among all types of motion.



It did not escape attention of Boltzmann, Maxwell, and others that equipartition theorem could give right answer if vibrational or rotation contributions to heat capacity were dropped. Boltzmann thought somehow energy couldn't transfer into molecular vibrations, but could not find suitable explanation.

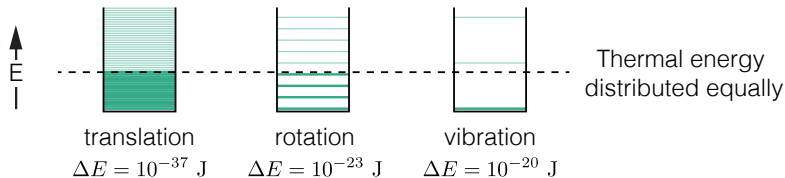
$$U_m = \underbrace{\frac{3}{2}RT}_{\text{trans}} + \underbrace{RT}_{\text{rot}} + \cancel{\underbrace{(6-5)RT}_{\text{vib}}}^0 = \frac{5}{2}RT = 20.79 \text{ J}/(\text{mol}\cdot\text{K})$$

Gas	$C_{V,m}$ (measured) / J/(mol·K)
H ₂	20.50
N ₂	20.50
O ₂	21.50

Heat capacity of a gas

Quantum Effects

- In quantum mechanics molecules can only be found in discrete energy states.
- Spacing between energy levels depends on type of motion: $\Delta E_{\text{trans}} < \Delta E_{\text{rot}} < \Delta E_{\text{vib}}$
- Spacings between vibrational energy levels, ΔE_{vib} , exceeds $k_B T$ at room temperature.

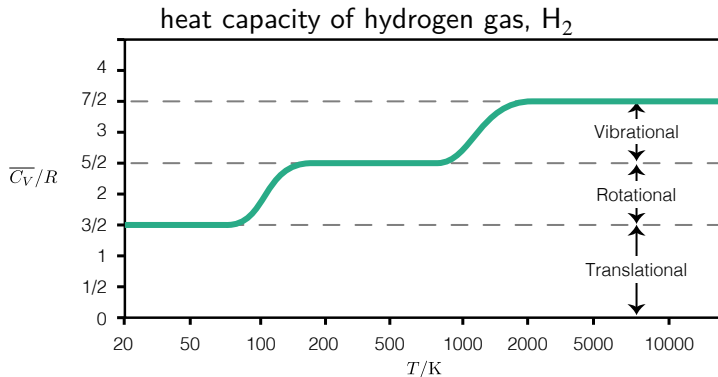


- Thermal energy at room temperature is not high enough to excite molecular vibrations.
- With no ability to excite diatomic or polyatomic molecule vibrations, gas has lower heat capacity than predicted—greater temperature increase for fixed amount of heat.

Heat capacity of a gas

Quantum Effects

- At even lower temperatures we can lose rotational motion contribution to heat capacity.
- Quantum effects lead to step-like heat capacity for gases as a function of temperature.



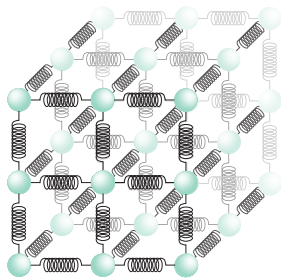
(note the logarithmic temperature scale)

Heat capacity of a solid

Heat capacity of a solid

We can use equipartition of energy theorem to predict heat capacity of solids.

- Unlike situation in gas phase, in solid phase we expect no translational motion.
- Let's also assume no rotational motion—may not be good assumption for molecular solids.
- Leaves only vibrational motion as the primary sink for thermal energy.



- Each atom in solid has vibrational energy motion in 3 dimensions giving 3 kinetic energy contributions and 3 potential energy contributions—each of which involve a squared coordinate.
- Equipartition of energy predicts average thermal energy per atom:

$$\bar{\epsilon} = 6 \left(\frac{1}{2} k_B T \right)$$

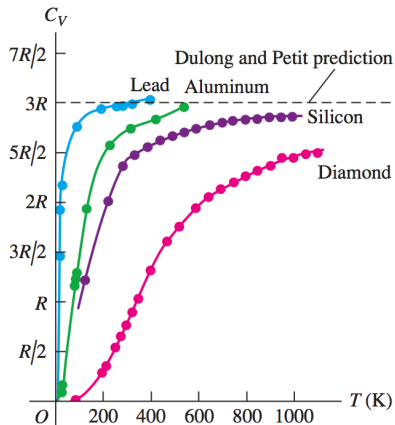
- For 1 mole of atoms in solid this predicts internal energy:

$$U_m = 3RT$$

Dulong and Petit rule for the heat capacity of a solid

Given $U_m = 3RT$ we obtain

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T} \right)_V = 3R \approx 25 \text{ J/(mol}\cdot\text{K)}, \quad \text{Dulong and Petit rule.}$$



Quantum effects cause the heat capacities of solids to decrease with decreasing temperature.

Why do different materials reach Dulong-Petit limit at different temperatures?

Heat capacity of a solid

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T} \right)_V = 3R \approx 25 \text{ J}/(\text{mol}\cdot\text{K})$$

Name	$C_p/\text{J}/(\text{mol}\cdot\text{K})$	Name	$C_p/\text{J}/(\text{mol}\cdot\text{K})$
Aluminum	24.20	Platinum	25.86
Antimony	25.23	Potassium	29.600
Arsenic	24.64	Praseodymium	27.20
Barium	28.07	Rhenium	25.48
Beryllium	16.443	Rhodium	24.98
Bismuth	25.52	Rubidium	31.060
Cadmium	26.020	Ruthenium	24.06
Calcium	25.929	Samarium	29.54
Carbon (graphite)	8.517	Scandium	25.52
Cerium	26.94	Selenium	25.363
Cesium	32.210	Silicon	19.99
Chromium	23.35	Silver	25.350
Cobalt	24.81	Sodium	28.230
Copper	24.440	Strontium	26.79
Gallium	26.03	Sulfur (rhombic)	22.70
Germanium	23.222	Tantalum	25.36
Gold	25.418	Tellurium	25.73
Iridium	25.10	Terbium	28.91
Iron	25.10	Thallium	26.32
Lead	26.84	Thorium	27.32
Lithium	24.860	Thulium	27.03
Magnesium	24.869	Tin (white)	26.99
Manganese	26.32	Titanium	25.060
Mercury	27.983	Tungsten	24.27
Molybdenum	24.06	Uranium	27.665
Neodymium	27.45	Vanadium	24.89
Nickel	26.07	Ytterbium	26.74
Niobium	24.60	Yttrium	26.53
Palladium	25.98	Zinc	25.390
		Zirconium	25.36