Molar Specific Heats of an Ideal Gas

- Molar Specific Heats

- Isovolumetric Processes

- Isobaric Processes

- Adiabatic Processes

- Equipartition of Energy

- Homework

Molar Specific Heats

- The energy required to raise the temperature of n moles of gas from T_i to T_f depends on the path taken between the initial and final states.

- Below is a PV diagram showing an isovolumetric process and an isobaric process that connect the same two isotherms.

- The energy transfer for the two processes can be written as

$$Q = nC_V\Delta T \qquad (constant\ volume)$$

$$Q = nC_p\Delta T \qquad (constant\ pressure)$$

where C_V is the molar specific heat at constant volume and C_P is the molar specific heat at constant pressure.

Serway/Jewett; Principles of Physics, 3/e
Figure 17.13
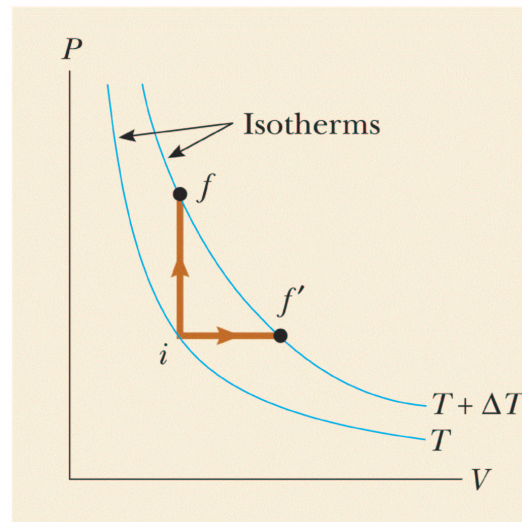
Isovolumetric Processes

- The first law of thermodynamics can be written in differential form as

$$dE_{int} = dQ + dW = dQ - PdV$$

- In an isovolumetric process $dV = 0$, so we have

$$dE_{int} = dQ = nC_V dT$$

- Thus, the change in internal energy be can be expressed as

$$\Delta E_{int} = nC_V \Delta T$$

  - Since the change in internal energy is a state variable it does not depend on the path taken between the initial and final states, and the above equation holds for any process in which the temperature change is ΔT.
  - Also, the above equation is valid for monatomic, diatomic, and polyatomic gases.

- The differential form of the equation can be used to express the molar specific heat at constant volume as

$$C_V = \frac{1}{n} \frac{dE_{int}}{dT}$$

Isobaric Processes

- Applying the first law to the isobaric process yields

$$dE_{int} = dQ - PdV = nC_PdT - PdV$$

- Using the ideal gas law, we can write $PdV = nRdT$

- Substituting this and $dE_{int} = nC_VdT$ into the expression for the first law gives

$$nC_VdT = nC_pdT - nRdT$$

$$C_P - C_V = R$$

- This expression applies to any ideal gas and shows that the molar specific heat at constant pressure is greater than the molar specific heat at constant volume by the amount R

Adiabatic Processes

- In an adiabatic process $dQ = 0$, so the first laws gives us

$$dE_{int} = -PdV$$

$$dE_{int} + PdV = 0$$

$$nC_V dT + \frac{nRT}{V}dV = 0$$

$$dT + \frac{R}{C_V}T\frac{dV}{V} = 0$$

$$dT + \frac{C_P - C_V}{C_V}T\frac{dV}{V} = 0$$

$$dT + \left(\frac{C_P}{C_V} - 1\right)T\frac{dV}{V} = 0$$

$$dT + (\gamma - 1)T\frac{dV}{V} = 0$$

where $\gamma = \frac{C_P}{C_V}$.

- Multiplying by $V^{\gamma-1}$ we have

$$V^{\gamma-1}dT + T(\gamma - 1)V^{\gamma-2}dV = 0$$

$$d\left(TV^{\gamma-1}\right) = 0$$

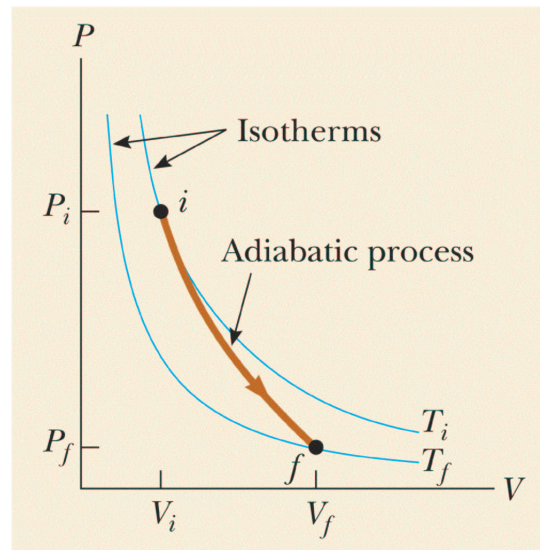$$TV^{\gamma-1} = constant$$

Adiabatic Process II

- From the previous expression, we can write

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

$$\frac{P_i V_i}{nR} V_i^{\gamma-1} = \frac{P_f V_f}{nR} V_f^{\gamma-1}$$

$$P_i V_i^{\gamma} = P_f V_f^{\gamma}$$

$$PV^{\gamma} = constant$$

- The PV diagram for an adiabatic expansion is shown below

Serway/Jewett; Principles of Physics, 3/e
Figure 17.14

Equipartition of Energy

- Consider a monatomic ideal gas undergoing an isovolumetric process

- We have shown that for an isovolumetric process the first law of thermodynamics becomes

$$Q = \Delta E_{int}$$

  and that for a monatomic gas

$$E_{int} = \frac{3}{2} nRT$$

- So, the first law yields

$$nC_V \Delta T = \frac{3}{2} nR\Delta T$$

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

- This prediction is in excellent agreement with measured values of C_V for monatomic gases, but fails for diatomic and polyatomic gases

TABLE 17.3	Molar Specific Heats of Various Gases			

	Molar Specific Heat $(J/mol \cdot K)$[a]			
	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

[a] All values except that for water were obtained at 300 K.

Equipartition of Energy II

- For diatomic and polyatomic molecules, we must take into account the other types of motion that exists in addition to translation

- The figure below shows the possible motions of a diatomic molecule: (a) translational, (b) rotational, and (c) vibrational

Serway/Jewett; Principles of Physics, 3/e
Figure 17.15
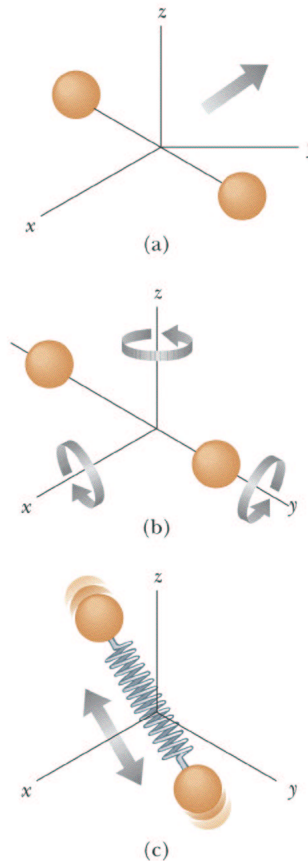
Equipartition of Energy III

- The theorem of equipartition of energy states that each degree of freedom, on average, contributes $\frac{1}{2}k_B T$ of energy per molecule

- If we consider the rotational motion of a diatomic molecule in addition to its translational motion, we get 5 degrees of freedom (rotation about the y axis shown below can be ignored because the moment of inertia is so small) which for a gas with N molecules yields

$$E_{int} = 5N\left(\frac{1}{2}k_B T\right) = \frac{5}{2}Nk_B T = \frac{5}{2}nRT$$

$$C_V = \frac{1}{n}\frac{dE_{int}}{dT} = \frac{5}{2}R = 20.8 \; J/mol \cdot K$$

$$C_P = C_V + R = \frac{7}{2}R$$

$$\gamma = \frac{C_p}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.40$$

- If we include the two degrees of freedom associated with the vibrational motion (one for the kinetic energy and one for the potential energy), we have

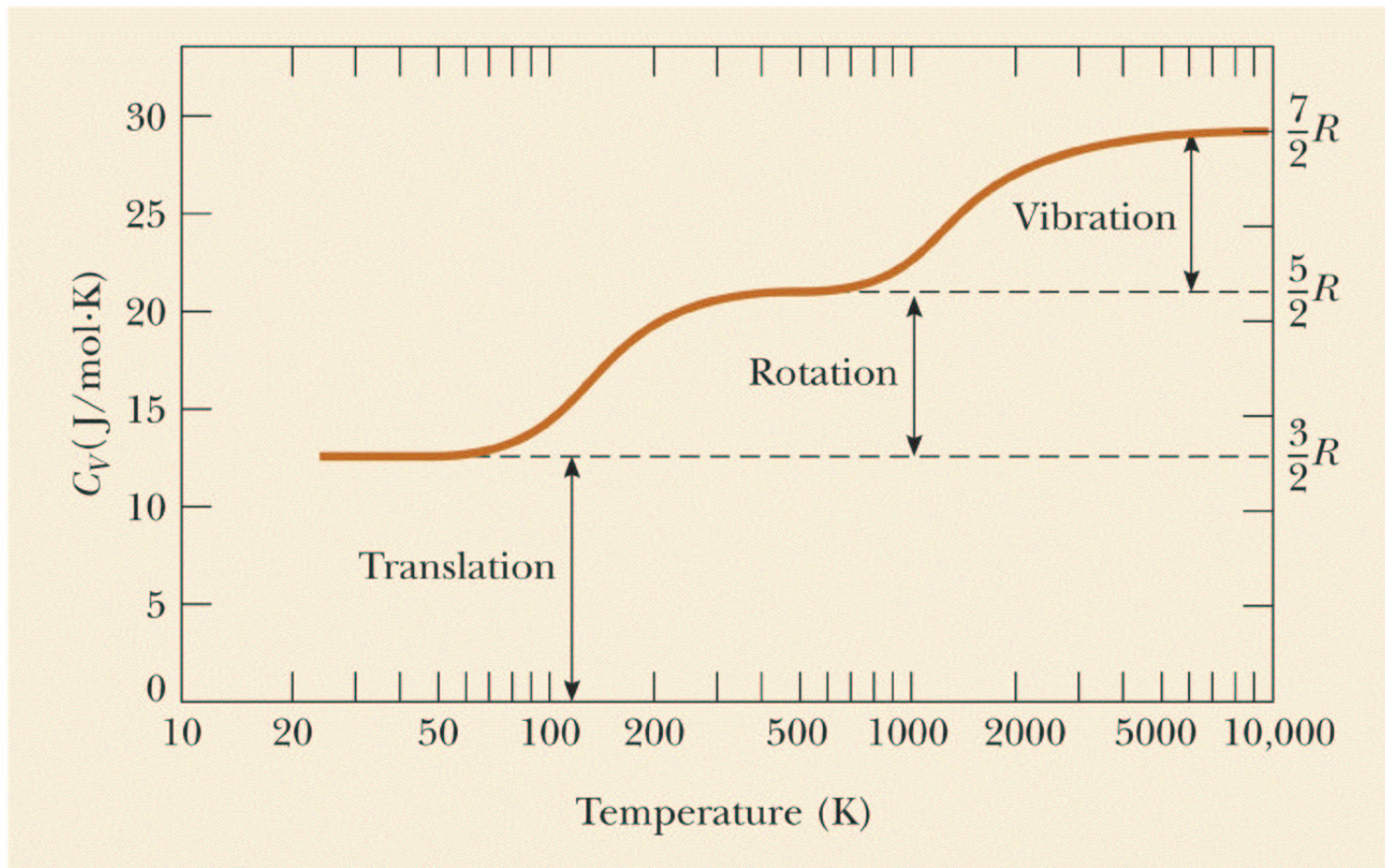$$E_{int} = 7N\left(\frac{1}{2}k_B T\right) = \frac{7}{2}Nk_B T = \frac{7}{2}nRT$$

$$C_V = \frac{1}{n}\frac{dE_{int}}{dT} = \frac{7}{2}R = 29.1 \; J/mol \cdot K$$

$$C_P = C_V + R = \frac{9}{2}R$$

$$\gamma = \frac{C_p}{C_V} = \frac{\frac{9}{2}R}{\frac{7}{2}R} = \frac{9}{7} = 1.29$$

Molar Specific Heat of Hydrogen vs. Temperature

A Hint of Quantum Physics

- Our classical model can't explain the temperature dependence of C_V shown on the previous slide

- To understand this behavior, we need to apply quantum theory in which energy is quantized

- The energy level diagram for the rotational and vibrational states of a diatomic molecule is shown below

- At low temperatures, all the molecules are in the ground state for rotation and vibration, and only the translational motion contributes to the molecules' average energy

- At higher temperatures, molecules are excited into rotational excited states and rotational motion contributes

- At still higher temperatures, vibrational excited states are populated and vibrational motion contributes
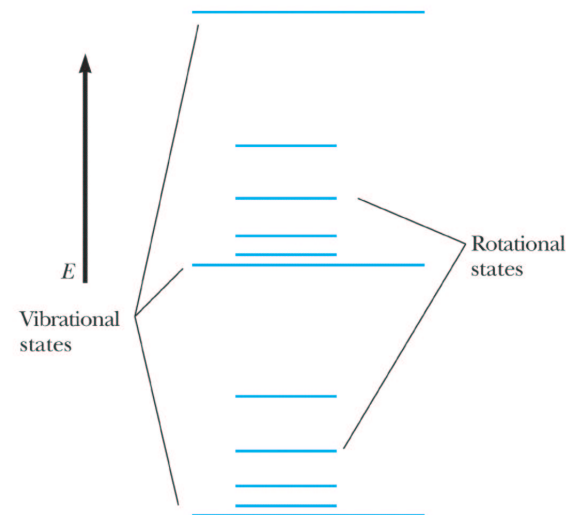
Example 1

A bubble of 5.00 mole of helium is submerged at a certain depth in liquid water when the water (and thus the helium) undergoes a temperature increase ΔT 0f 20.0°C at constant pressure. As a result, the bubble expands. The helium is monatomic and ideal. (a) How much energy is added as heat to the helium during the temperature increase and expansion? (b) What is the change in the internal energy of the helium? (c) How much work is done on the helium?

Example 2

One mole of a diatomic ideal gas at a temperature of 310 K expands adiabatically from an initial volume of 12.0 L to a final volume of 19.0 L. What is the final temperature of the gas?

Homework Set 6 - Due Wed. Jan. 21

- Read Sections 17.7 - 17.9
- Do Problems 17.32, 17.35, 17.36, 17.40 & 17.42