Reese Ch. 14, part B (pp. 649-658)

- Degrees of Freedom and Equipartition
- Specific Heat of a Solid
- Quantum Effects
- Adiabatic Processes

Degrees of Freedom

- In advanced mechanics, the number of degrees of freedom of a system is the number of independently specifiable coordinates. However, in discussions of thermal physics, **the number of degrees of freedom of a system is the number of different terms that must be added up to obtain the energy of the system.** For example, each "molecule" in a monatomic gas has 3 degrees of freedom, corresponding to $E = KE = \frac{1}{2}\mu v_x^2 + \frac{1}{2}\mu v_y^2 + \frac{1}{2}\mu v_z^2$

Equipartition of Energy

- One mole of a monatomic gas has $3N_A$ degrees of freedom.
- An important concept in thermal physics is the theorem of equipartition of energy: that in equilibrium the total energy of the system is divided equally among all its degrees of freedom. (There are limitations on this theorem, the most important of which is that only the active degrees of freedom share in the equipartition.)
- Since a monatomic gas has a total energy of $\frac{3}{2}N_A kT$ each degree of freedom accounts for

$$\frac{1}{2}kT$$

Specific Heat of a Monatomic Solid: I

- In the simplest model of an monatomic solid, there are 6 active degrees of freedom per atom: 3 kinetic-energy terms and 3 quadratic potential-energy terms. The molar specific heat at constant volume should therefore be

$$c_V \equiv \frac{1}{n}\left(\frac{dU}{dT}\right)_V = 6(\frac{1}{2}R) = 3R = 24.95 J/(mol \cdot K)$$

- This "law of Dulong and Petit" was discovered experimentally in the early 1800's.

Specific Heat of a Monatomic Solid: II

- The law of Dulong and Petit does not apply to molecular solids, and it does not even apply to monatomic solids at very cold temperatures. This reflects the fact that the rule of equipartition only applies to active degrees of freedom.
- Understanding the low-temperature behavior of the specific heat of a monatomic solid requires the use of "quantum statistical mechanics," in which the quantum mechanical nature of atomic and molecular systems is incorporated. Albert Einstein and Peter Debye did such work soon after the development of quantum mechanics.
- The failure of classical statistical mechanics to account for low-temperature specific heats of atomic solids is just one of its failures. Other serious failures occur with gases ….

Don't Atoms Rotate?: I

- A classical picture of a monatomic ideal gas would presumably assign a tiny but finite radius to each individual atom. Such atoms should be capable of rotation, and each rotational degree of freedom should have $\frac{1}{2}kT$ of energy. This would make the molar specific heat twice as big as it is measured to be!

Don't Atoms Rotate?: II

- This conundrum is resolved by quantum mechanics, according to which the atom consists of a nucleus surrounding by a cloud of electrons. Although electrons (and nuclei) do have angular momentum, quantum mechanics reveals that only certain angular momentum values are allowed, and that these allowed "states" correspond to certain definite energy values that are separated by energies large compared to kT for typical laboratory temperatures.
- Therefore these intra-atomic degrees of freedom are not active but are **frozen out at ordinary temperatures**. At sufficiently high temperatures, electronic excitations can contribute to the internal energy (and therefore to the specific heats).

Diatomic Gases: Rotation

- The transition from quantum freezing to classical equipartition can be seen in the behavior of the specific heat of a diatomic gas. Because a diatomic gas has a nonnegligible moment of inertia about two axes, it should have 2 rotational degrees of freedom, so its molar specific heat "should be" $\boxed{c_V = \frac{5}{2}R}$
- At low temperatures the specific heat of a typical diatomic gas is found to be only 1.5R, but as the gas is warmed toward room temperature, the specific heat climbs to 2.5R.
- This occurs when as kT gets large enough compared to the (temperature-independent) spacing between the adjacent rotational levels.

Diatomic Gases: Vibration

- At even higher temperatures, 2 more degrees of freedom thaw out: these are the kinetic energy and potential energy of molecular vibration, in which the "spring" (the bond between the two atoms of the molecule) is alternately stretched and compressed.
- When kT gets to be larger than the spacing of adjacent molecular quantum states, the molar specific heat of a diatomic gas rises from 2.5R to 3.5R, corresponding to 7 active degrees of freedom per molecule.
- The vibrational thawing occurs at a higher temperature than the rotational thawing, with the exact transition temperatures depending on the masses of the two atoms, their equilibrium separation (bond length), and the stiffness of the spring (bond).

Polyatomic Gases

- The details for polyatomic molecules are complicated by the presence of multiple "springs" (atom-atom bonds), but again the specific heat rises as rotational degrees of freedom (how many?) and then vibrational degrees of freedom thaw out as the temperature is raised.
- At room temperature, the molar specific heat c_V of a typical polyatomic molecule is between greater than 3R.

Adiabatic Processes

An adiabatic process is one in which there is zero heat transfer between the system and its surroundings. This means that the internal energy change equals the negative of the work done by the system on its surroundings:

$$\Delta U = -W_{by}$$

Adiabatic Expansion: Ideal Gas: I

- When a gas expands adiabatically, its internal energy an amount equal to the PdV work done by the gas on its surroundings. A careful analysis shows that it an (infinitesimal) adiabatic expansion of an ideal gas, the temperature obeys

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

and the pressure obeys $\frac{dP}{P} = -\gamma \frac{dV}{V}$

Here $\gamma \equiv c_P / c_V$ the ratio of specific heats. Note: $\gamma > 1$

Adiabatic Expansion: Ideal Gas: II

- In a finite adiabatic expansion, as long as the specific heats remain constant throughout the expansion, the equations for dT and dP on the previous slide can be integrated to give:

$$TV^{\gamma-1} = \text{constant} = T_i V_i^{\gamma-1}$$

$$PV^{\gamma} = \text{constant'} = P_i V_i^{\gamma}$$

- The specific heats ratio γ is often referred to as the adiabatic exponent.
- STP values of γ: 5/3=1.67 for helium; 7/5=1.40for N_2