Heat Capacities, Absolute Zero, and the Third Law

- We have already noted that heat capacity and entropy have the same units.
- We will explore further the relationship between heat capacity and entropy.
- We will see that entropy is absolute and explore the Third Law of Thermodynamics.

Variation of Entropy with Temperature

• Consider:

$$dS = \frac{dq_{rev}}{T}$$

• We have considered constant V and constant P paths, respectively:

$$C_V = \frac{dq_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$$
$$C_P = \frac{dq_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$$

• Therefore

$$dS_V = \frac{C_V}{T} dT = \left(\frac{\partial S}{\partial T}\right)_V dT$$
$$dS_P = \frac{C_P}{T} dT = \left(\frac{\partial S}{\partial T}\right)_P dT$$

• Heat capacities are temperature dependent:

$$\Delta S_V = \int_{T_i}^{T_f} \frac{C_V(T)}{T} dT$$
$$\Delta S_P = \int_{T_i}^{T_f} \frac{C_P(T)}{T} dT$$

Absolute Zero

- Consider 10 identical bricks beside a table of height h.
- If they are initially at h = 0, then the internal energy is U(n = 0), where n is the number of bricks on the table.
- If n bricks are on the table, then the change in internal energy is:

$$\Delta U(n) = U(n) - U(n = 0) = nMgh = n\epsilon$$

where:

$$\epsilon = Mgh$$

- 1 way to have n = 0.
- 10 ways to have n = 1.
- 45 ways to have n = 2.

- ÷
- W(n) ways to have n = n where

$$W(n) = \frac{N!}{n!(N-n)!}$$

- Each specific arrangement is a microstate of the system.
- The entropy associated with the state of the system is:

$$S(n) = k_B \ln W(n)$$

- Therefore, the more microscopic states that correspond to a particular macrostate characterized by macroscopic variables (such as P, V, T, U, and S), the greater the entropy.
- Now split the set of ten bricks into two subsystems, each consisting of five bricks.
 - One set of bricks is on the table $(U = 5\epsilon)$.
 - One set of bricks is on the floor (U = 0).
 - Bring the two systems together. Therefore $U = 5\epsilon$.
- But we still know which five bricks are on the table and which five are on the floor.
- Supposed that there existed an "interbrick force" by which bricks could trade places.
 - Therefore there will still be five bricks on the table and five bricks on the floor (and $U = 5\epsilon$), but we know longer know which bricks are where.
- This is what happens with molecules. There is chaotic redistribution of molecules among microstates corresponding to the observed macrostate.
- Now consider molecules instead of bricks in the case where there are only two energy levels available for each molecule (i.e. a two level system).
 - The lower level has an energy of 0 and the higher level has an energy of ϵ .
 - Therefore, for the system:

$$\Delta U(n) = U(n) - U(n=0) = n\epsilon$$

and

$$\Delta S(n) = S(n) - S(n=0) = k_B \ln\left(\frac{N!}{n!(N-n)!}\right)$$

- Consider U(n) plotted against S(n) (Figure 4.2)
- Now remember the Master Equation:

$$dU = TdS - PdV$$

• Therefore:

$$\left(\frac{\partial(\Delta U(n))_V}{\partial(\Delta S(n))}\right)_V = \left(\frac{\partial U(n)}{\partial S(n)}\right)_V = T(n)$$

• Applying the chain rule:

$$\left(\frac{\partial U(n)}{\partial S(n)}\right)_{V} = \left(\frac{\partial U(n)}{\partial n}\right)_{V} \left(\frac{\partial n}{\partial S(n)}\right)_{V}$$

$$= \left(\frac{\partial U(n)}{\partial n}\right)_{V} \left(\frac{\partial S(n)}{\partial n}\right)_{V}^{-1}$$

- Since $U(n) = n\epsilon$, $(\partial U(n)/\partial n)_V = \epsilon$
- Now for $(\partial S(n)/\partial n)_V$:
 - Need to use Stirling's approximation for very large N:

$$\ln N! = N \ln N$$

• With Stirling's approximation:

$$\Delta S(n) = k_B \ln \left(\frac{N!}{n!(N-n)!} \right)$$
$$= k_B \left[\ln N! - \ln n! - \ln(N-n)! \right]$$
$$\cong k_B \left[N \ln N - n \ln n - (N-n) \ln(N-n) \right]$$

 $\bullet\,$ we find:

$$\left(\frac{\partial S(n)}{\partial n}\right)_V = k_B \ln\left(\frac{N}{n} - 1\right)$$
$$T(n) = \frac{\epsilon}{k_B \ln\left(\frac{N}{n} - 1\right)}$$

Therefore:

What is the limiting behaviour of this function?

- If $n \to 0$ then $T(n) \to 0$.
 - All the molecules are in their lowest state.
 - Internal energy at its lowest value.
 - Entropy at its lowest value.
- If $n \to N/2$ then $T(n) \to \infty$
 - Molecules evenly split between the two levels.
 - Entropy at its maximum value.
- Rearrange

$$T(n) = \frac{\epsilon}{k_B \ln\left(\frac{N}{n} - 1\right)}$$

 to

$$\ln\left(\frac{N}{n}-1\right) = \frac{\epsilon}{k_B T}$$
$$\ln\left(\frac{N-n}{n}\right) = \frac{\epsilon}{k_B T}$$
$$\ln\left(\frac{n}{N-n}\right) = -\frac{\epsilon}{k_B T}$$
$$\left(\frac{n}{N-n}\right) = e^{-\epsilon/k_B T}$$

(also known as the Boltzmann distribution)

- Consider the following two questions:
 - Are there real molecular systems with only two energy levels?
 - What about the dashed part of figure 4.2? If n > N/2, then the temperature would be negative!
- Consider a two level molecular systems:
 - For example, consider nuclear spin, which is either "up" or "down".
 - These levels are degenerate (i.e. have the same energy) if there is no external field.
 - If there is an external field, the energy levels are different.
 - Negative temperatures occur only in systems with very few energy levels.
 - Negative temperature systems are "hotter" than positive temperature systems associated with population inversions where the higher energy state is more populated than the lower energy level.
 - Population inversions are essential for the operation of lasers.
- It is 1/T that characterizes the degree of "hotness".
 - $-1/T \rightarrow -\infty$ (Coldest system)
 - $-1/T \rightarrow 0$
 - $-1/T \to \infty$ (Hottest system)

More about heat capacity

• Recall:

$$T(n) = \frac{\epsilon}{k_B \ln\left(\frac{N}{n} - 1\right)}$$

• which was rearranged to:

$$\left(\frac{n}{N-n}\right) = e^{-\epsilon/k_B T}$$

• Solving for n gives:

$$n = N \frac{e^{-\epsilon/k_B T}}{1 + e^{-\epsilon/k_B T}} = N \frac{e^{-x}}{1 + e^{-x}}$$

where $x = \epsilon / kBT$.

• Therefore:

$$U(T) = n\epsilon = N\epsilon \frac{e^{-x}}{1 + e^{-x}}$$

and

$$C_V = \left(\frac{\partial U(T)}{\partial T}\right)_V = Nk_B x^2 \frac{e^{-x}}{(1+e^{-x})^2}$$

- Figure 4.4 shows heat capacity as a function of temperature.
- Heat capacity increases then decreases.
- Once a molecule is in the upper of the two states, how can it be further excited?
- Real molecules have many states.
 - Therefore heat capacity increases with temperature.
 - As temperature increases more energy levels (and other types of energy levels) become available.

Heat Capacity of Solids

• Dulong and Petit (1819) observed that \overline{C}_V for atomic solids was independent of temperature and was approximately the same for a wide range of atomic solids.

$$\overline{C}_V = 3R$$

- This can be interpreted in terms of the vibrations of the atoms within the atomic crystal with each direction (x, y, z contributing R to the molar heat capacity.
- Kopp (1865) devised an empirical scheme for estimating heat capacities of polyatomic solids with the contribution of each atom empirically determined (Table 4.1).
 - The values for \overline{C}_V range from 0.9R for a carbon atom to 3.02R for other atoms. It works reasonably well.
- How does heat capacity vary with temperature as $T \rightarrow 0$?

Heat Capacity at Low Temperatures

- Recall that the temperature dependence of heat capacity depends roughly on the magnitude of k_BT relative to the spacing of quantum levels.
 - If the spacing is "too big" that degree of freedom is not "active" at that temperature.
 - Therefore we hypothesize that heat capacity approaches zero as T approaches zero.
- Debye (1912) modified Einstein's theory (1907).
 - Debye's Law is:

$$\frac{\overline{C}_V}{R} = \frac{12\pi^4}{5} \left(\frac{T}{\Theta_D}\right)^3$$

where Θ_D is the Debye temperature.

- The Debye temperature is related to nuclear motions in the solid and thus the nature of the metal with soft metals having lower Θ_D than harder metals.
- Electronic states also can contribute to the heat capacity of a metal, but in a different way than do nuclear motions.
 - For electrons:

$$\frac{\overline{C}_V}{R} = \frac{T}{\Theta_{el}}$$

• Thus the total heat capacity of a metal is:

$$\frac{\overline{C}_V}{R} = \frac{T}{\Theta_{el}} + \frac{12\pi^4}{5} \left(\frac{T}{\Theta_D}\right)^3$$

Heat Capacity of Liquids

- In a liquid the molecules are no longer constrained to motion about one particular site.
- Therefore the heat capacity of a liquid is greater than the heat capacity of a solid.
- The heat capacity of a liquid is also greater than that of a gas because of the proximity of the molecules to each other.
- Heat capacities of liquids are empirically determined and are typically around 9R for small molecules.

• For larger molecules, internal degrees of freedom must be considered and the heat capacity is larger.

Heat Capacity of Gases

- Depends on internal structure of the gas.
- If there are N atoms in the gas there are:
 - Three translational degrees of freedom, each contributing R/2 to C_V .
- If the molecule is linear, then there are:
 - 2 rotational degrees of freedom, each contributing R/2 to C_V .
 - 3N-5 vibrational degrees of freedom, each contributing R to C_V .
- If the molecule is nonlinear, then there are:
 - 3 rotational degrees of freedom, each contributing R/2 to C_V .
 - 3N 6 vibrational degrees of freedom, each contributing R to C_V .
- This is assuming all degrees of freedom are active.
- Heat capacity for gases is determined empirically and is usually expressed as:

$$\frac{C_p(T)}{R} = a + bT + cT^2 + dT^3$$

- We must now consider the relationship between C_V and C_P .
 - Recall

$$C_P - C_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

 $\overline{C}_P - \overline{C}_V = \frac{TV\alpha^2}{\kappa}$

which leads to:

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

and

where

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

- $\bullet\,$ In the adiabatic expansion, we encountered the ratio γ .
 - For an ideal gas $\gamma = 5/3$.
- Without using the ideal gas equation of state, it can be shown that $\gamma = C_P/C_V$.
- Assuming that $C_P C_V = nR$, γ for a polyatomic molecule can indicate the number of atoms and whether the molecule is linear.
 - For a monatomic gas:

$$\gamma = \frac{5}{3}$$

• For a linear molecule in the gas phase:

$$\frac{7}{5} \ge \gamma \ge \frac{6N-3}{6N-5}$$

• For a nonlinear molecule in the gas phase:

$$\frac{4}{3} \ge \gamma \ge \frac{6N-4}{6N-6}$$

• The relationship

$$\overline{C}_P - \overline{C}_V = \frac{TV\alpha^2}{\kappa}$$

is important for condensed phases.

- α is T dependent for both solids and liquids. Typical values are approximately 10^{-5} K⁻¹ for solids and 10^{-3} to 10^{-4} K⁻¹ for liquids.
- κ is not strongly T dependent for and is about 10^{-6} atm⁻¹ for metals and 10^{-4} atm⁻¹ for molecular solids.
- Recall

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

- Since U is a state function, it has an exact differential.
 - Therefore:

$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T} \right) = \frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)$$

• But:

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

and:

$$\begin{split} \frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right) &= \frac{\partial}{\partial T} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] \\ &= T \left(\frac{\partial^2 P}{\partial T^2} \right)_V \\ &\left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V \end{split}$$

• Following the same procedure, but starting with H it may be shown that:

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

- We have now considered the heat capacity of solids, liquids, and gases.
- We already know how to calculate entropy changes from heat capacity.
- In order to calculate absolute entropy starting from absolute zero to the temperature of interest, we must now consider the entropy of phase changes.

Phase Transitions

- Some common phase transitions are:
- Solid to solid, i.e. from one crystalline state to another

- H₂O ice I to ice II
- rhombic S to monoclinic S
- $\bullet\,$ Fe phase 1 and Fe phase 2
- Solid to liquid (fusion)
- Solid to gas (sublimation)
- Liquid to gas (vaporization)
- During a phase transition, heat is transferred into or out of the system without changing the temperature.
 - Since constant P conditions are more easily maintained than constant V conditions, q_P , is usually measured.

Fusion of water

- Consider one mole of ice at 273.15 K and 1 atm.
- Transfer energy until ice melts leaving one mole of water.

 $H_2O(s, 1 \text{ atm}, 273.15 \text{ K}) \longrightarrow H_2O(l, 1 \text{ atm}, 273.15 \text{ K})$

• The associated heat transfer is:

$$q = q_P = \Delta \overline{H} = \Delta \overline{H} (\text{water}) - \overline{H} (\text{ice})$$

which is the enthalpy change of fusion, $\Delta \overline{H}_{fus}$, (also known as the heat of fusion).

- The standard enthalpy of fusion, $\Delta \overline{H}_{fus}^{\circ}$, is defined with respect to the pressure of 1 bar (**not 1 atm**).
- Similarly defined is the standard enthalpy of vaporization, $\Delta \overline{H}_{vap}^{\circ}$.
- For a given substance, $\Delta \overline{H}_{vap}^{\circ}$ is usually greater than $\Delta \overline{H}_{fus}^{\circ}$.
 - This is because fusion involves partially overcoming intermolecular interactions while vaporization involves completely overcoming intermolecular interactions.
- If a substance goes directly from the solid to the gas phase, the process is called sublimation and $\Delta \overline{H}_{sub}^{\circ}$ is the corresponding standard enthalpy.
- There are also solid-solid phase transitions between different solid crystalline forms.
 - Associated standard enthalpies tend to be small.

Entropy of Phase Transitions

- During a phase transition at constant T and P, both phases are in equilibrium with each other.
 - For a general phase transition, ϕ ,

$$\Delta S_{\phi} = \frac{q_{\phi}}{T_{\phi}} = \frac{\Delta H_{\phi}}{T_{\phi}}$$

• Standard entropies of phase transitions for water are:

$$\Delta S_{vap}^{\circ} = \frac{\Delta H_{vap}^{\circ}}{T_{vap}} = 13.10R$$
$$\Delta S_{fus}^{\circ} = \frac{\Delta H_{fus}^{\circ}}{T_{fus}} = 2.65R$$

The Third Law and Absolute Entropy

- Absolute entropy can be assigned to any state.
 - Recall the bricks and the microstate where all the bricks were on the floor (or n = 0).

$$W(n=0) = \frac{N!}{0!N!} = 1$$

• Therefore:

$$S(n = 0) = k_B \ln W(n = 0) = 0$$

- Since the definition of W does not involve a reference state, the corresponding entropy is absolute.
- For a molecular system, all the bricks on the floor would correspond to the molecules arranged in a perfect crystal.

Statements of the Third Law

- "At absolute zero, the entropy of every perfect crystalline equilibrium compound is zero."
- "The entropy of any equilibrium system is zero for the state in which $(\partial U/\partial S)_V = 0$."
- "The isotherm T = 0 and the isentrope S = 0 are the same."
- "It is impossible to attain absolute zero by any process with a finite number of steps."
- Therefore it is impossible to reach absolute zero.

Calculation of Absolute Entropy

• Consider entropy:

$$dS_V = \frac{C_V(T)}{T} dT$$
$$dS_P = \frac{C_P(T)}{T} dT$$

• Consider the entropy change at constant pressure from T_i and T_f :

$$\Delta S = S(T_f) - S(T_i) = \int_{T_i}^{T_f} \frac{C_P(T)}{T} dT$$

- This would be fine if there were no phase transitions.
 - Entropy changes due to phase changes must be explicitly considered.
- If the change from T_i and T_f involves a phase transition from phase I to phase II at T_{ϕ} :

$$\Delta S = S(T_f) - S(T_i)$$
$$= \int_{T_i}^{T_\phi} \frac{C_P^I(T)}{T} dT + \frac{\Delta H_\phi}{T_\phi} + \int_{T_\phi}^{T_f} \frac{C_P^{II}(T)}{T} dT$$

- If $T_i = 0$ and every phase transition is considered, absolute entropy of any pure substance at any temperature may be determined.
- Your text works an example for O₂.

Here ends Chapter 4