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 $n = 2$.

$\vdots$

- $W(n)$ 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:

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

$$= k_B \left[\ln N! - \ln n! - ln(N-n)!\right]$$

$$\cong k_B \left[N \ln N - n \ln n - (N-n)\ln(N-n)\right]$$

    - we find:

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

Therefore:

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

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)
  - $-1/T \rightarrow 0$
  - $-1/T \rightarrow \infty$ (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

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

which leads to:

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

where

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

and

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

- 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:
  $$\frac{7}{5} \geq \gamma \geq \frac{6N-3}{6N-5}$$
  - For a nonlinear molecule in the gas phase:
  $$\frac{4}{3} \geq \gamma \geq \frac{6N-4}{6N-6}$$
- 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:

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

- 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
  - H_2O ice I to ice II
  - rhombic S to monoclinic S
  - 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.

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

- 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, $\Delta\overline{H}^{\circ}_{fus}$, is defined with respect to the pressure of 1 bar (**not 1 atm**).
- Similarly defined is the standard enthalpy of vaporization, $\Delta\overline{H}^{\circ}_{vap}$.

- For a given substance, $\Delta\overline{H}^{\circ}_{vap}$ is usually greater than $\Delta\overline{H}^{\circ}_{fus}$.
  - 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 $\Delta\overline{H}^{\circ}_{sub}$ 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:

$$\Delta S^\circ_{vap} = \frac{\Delta H^\circ_{vap}}{T_{vap}} = 13.10R$$

$$\Delta S^\circ_{fus} = \frac{\Delta H^\circ_{fus}}{T_{fus}} = 2.65R$$

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 O_2.

Here ends Chapter 4