Content & Objectives: Chapters 6 and 7 concern entropy and its calculation in ideal gas systems. Chapter 6 discusses the need for a thermodynamic state function capable of predicting the direction of natural processes. The 2nd Law introduces such a function, the entropy, which provides a criterion for spontaneity and equilibrium in isolated systems. We will discuss the microscopic basis for entropy (i.e. the relationship to “disorder”) but the emphasis in Chapter 6 will be on the thermodynamic consequences of the 2nd Law, mainly using ideal gases for illustration. The 3rd Law, which establishes an absolute scale for entropy, is discussed in Chapter 7. Here we will look at the statistical mechanical calculation of absolute entropies of ideal gases in order to better understand the nature of entropy, as well as discuss how standard entropies are obtained from calorimetric data.

Reading: M&S Chapters 5-6, MathChapter E

Other Sources:
- 2nd Law: Rock Ch. 4; Carrington Ch. 6
- 3rd Law and Statistical Calculations: Rock Ch. 6 & 14; Pitzer Chapters 5-6

Entropy and The 2nd Law

- Numerous experimental observations suggest a fundamental directionality to natural processes. Historically, these observations were summarized in terms of restrictions on the operation of heat engines. Two famous statements of the 2nd Law can be paraphrased:
  
  **Clausius Statement** (1850): No engine working in a cycle can transfer energy from a cold body to a hot body and have no other effect.

  **Planck-Kelvin Statement** (1851): It is impossible to construct a device which operates in a cycle and has no other effect than to produce work by extracting heat from a reservoir at a single temperature.

- The modern statement of the 2nd **Law of Thermodynamics** we will employ is

  There exists an extensive state function of a system, termed the entropy, $S$, such that for any change in thermodynamic state

  $$dS \geq \frac{\delta q}{T},$$

  where the equality applies only if the change is carried out reversibly.

Note the importance of the concept of reversibility in this statement. Recall that a **reversible** (or quasi-static) process is one in which the system evolves through a succession of quasi-equilibrium states. To be truly reversible a process must be carried out infinitely slowly. All real processes are therefore irreversible to some extent.
For any process one can rewrite the “Clausius inequality” of the 2nd Law as an equality by introducing the idea of entropy production

\[ dS = \delta S_{\text{prod}} + \frac{\delta q}{T} \]

\( \delta S_{\text{prod}} \) is the entropy generated during a process via the creation and dissipation of gradients in temperature or pressure, by frictional effects, etc. In an (idealized) reversible process, wherein such effects are completely eliminated,

\[ dS = \frac{\delta q_{\text{rev}}}{T} \]

Many real processes can be treated as being reversible to a good approximation. In addition, even if the process of interest is not reversible, it is often useful to calculate the entropy change between the endpoints of the process using this expression for some reversible path.

### Interpretations of Entropy and Irreversibility

- The 1st Law establishes the “equality” of work and heat as forms of energy whereas the 2nd Law recognizes the differential utility (“quality”) of these energy forms. Mechanical work can be viewed as the coherent (ordered) motions of molecules, whereas heat involves chaotic (disordered) motion.

- The fundamental irreversibility of all natural processes (“time’s arrow”) stems from the fact that change in the direction order \( \rightarrow \) disorder is overwhelmingly more probable than is the reverse process.

- The physical principle behind the 2nd Law is that energy tends to disperse – both spatially and in terms of its coherence (Atkins).

- Clausius (1865) succinctly summarized the 1st and 2nd Laws in the statement: “The energy of the universe is constant; the entropy tends toward a maximum.”

- The statistical mechanical interpretation of entropy in an isolated system is:

\[ S(N,V,U) = k_B \ln \Omega(N,V,U) \]

where \( \Omega(N,V,U) \) is the number of quantum states (each equally probably) consistent with the macroscopic constraints of fixed \( N, V \), and \( U \).

- More generally the entropy can be expressed in any ensemble by:

\[ S = -k_B \sum_{i} p_i \ln p_i \]

### General Consequences of the 2nd Law

- In an isolated system, \( \delta q = 0 \) and the system entropy provides a criterion for spontaneity and equilibrium:

\[ dS > 0 \text{ for any spontaneous process in an isolated system} \]

\[ dS = 0 \text{ for a isolated system at equilibrium} \]
i.e. isolated systems evolve towards a state of maximal entropy.

- Engines, refrigerators, and heat pumps are devices that operate in a cyclic manner to effect transformations between work and heat. Such devices are maximally efficient when run reversibly. For reversible operation, efficiency is limited solely by the two temperatures between which the device operates. Simple analysis based on combined application of the 1st and 2nd Laws to one cycle of operation of the device “D”

\[
\Delta U_D = w + q_H^{\text{rev}} + q_L^{\text{rev}} = 0 \quad (1\text{st Law}) \\
\Delta S_D = \frac{q_H^{\text{rev}}}{T_H} + \frac{q_L^{\text{rev}}}{T_L} = 0 \quad (2\text{nd Law})
\]

provides the theoretical maximum efficiencies shown in the following schematic.

**Efficiencies of Thermodynamic Devices**

**D = Heat Engine**

\begin{align*}
\text{Efficiency} & \equiv \frac{-w}{q_H} = \frac{T_H - T_L}{T_H} \\
\text{source} & \\
\text{exhaust} &
\end{align*}

**D = Refrigerator, Heat Pump, Air Cond.**

\begin{align*}
q_H & \quad q_L \\
T_H & \quad T_L \\
\text{kitchen} & \quad \text{house} & \quad \text{outdoors} \\
\frac{q_L}{w} & \quad \frac{-q_H}{w} & \quad \frac{q_L}{w} \\
\frac{T_H - T_L}{T_H - T_L} & \quad \frac{T_H - T_L}{T_H - T_L} & \quad \frac{T_L}{T_H - T_L} \\
\text{ice box} & \quad \text{outdoors} & \quad \text{house}
\end{align*}

Real devices have smaller efficiencies than these limiting values and can only approach them when sources of entropy production are minimized.

Note that these limiting thermodynamic efficiencies are completely independent of the particulars of the devices; they depend only on the ratio of the two temperatures involved. Such efficiencies can therefore used to establish the true thermodynamic scale of temperature.
### The Combined 1st and 2nd Laws and Entropy Changes

- For a reversible change in which only $PV$ work is performed, $\delta_{rev} = -PdV$ and the 1st Law can be written $dU = \delta_{q_{rev}} - PdV$. Furthermore, for a reversible process the 2nd Law states that $\delta_{q_{rev}} = TdS$, so that a combination of the two laws leads to:

  $$dU = TdS - PdV$$

  This equation shifts attention away from the “process” orientation of the 1st and 2nd Laws and places it on the state functions of a system in equilibrium. (The “rev” subscript is therefore irrelevant and omitted here.)

- Using this relation one can easily determine how entropy changes with $T$, $V$, and $P$:

  $$dS = \frac{C_V}{T}dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]dV$$

  $$dS = \frac{C_P}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

  Of most interest now are the relations:

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

  $$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

  which allow one to determine isochoric or isobaric changes in $S$ with $T$ based on a knowledge of $C_V(T)$ or $C_P(T)$.

### Entropy Changes in Ideal Gases

- For an ideal gas $(\partial U / \partial V)_T = (\partial H / \partial P)_T = 0$ so that for any reversible process the above equations for $dS$ can be simplified to:

  $$dS^{IG} = \frac{C_V}{T}dT + \frac{nR}{V}dV$$

  $$dS^{IG} = \frac{C_P}{T}dT - \frac{nR}{P}dP$$

- For a **reversible isothermal expansion**: $\Delta S^{IG} = nR\ln(V_2 / V_1) = -nR\ln(P_2 / P_1)$

- For a **reversible adiabatic expansion** $\Delta S = 0$. (Any reversible adiabatic expansion, whether of an ideal gas or not, is a constant entropy or isentropic process.)

- If $C_V$ is independent of temperature (as for a monatomic ideal gas) one has:

  $$S^{IG}(T_2, V_2) - S^{IG}(T_1, V_1) = C_V \ln(T_2 / T_1) + nR \ln(V_2 / V_1)$$

  $$S^{IG}(T_2, P_2) - S^{IG}(T_1, P_1) = C_P \ln(T_2 / T_1) - nR \ln(P_2 / P_1)$$

- Mixtures of ideal gases provide an important reference for thinking about mixtures of real substances. A result known as **Gibbs’ theorem** states that the entropy of a mixture of ideal gases at a given $T$ and some total $V$ is the sum of the entropies that each gas would have if it alone were to occupy the total volume $V$. Using this result, the isothermal mixing of ideal gases results in an **entropy of mixing**

  $$\Delta_{mix}S^{IG} \equiv \bar{S}(\text{mixture}) - \sum_i y_i \bar{S} (\text{pure } i) = - R \sum_i y_i \ln y_i$$
were \( y_i \) is the mole fraction of species \( i \).

---

**The 3rd Law of Thermodynamics & “Practical Absolute Entropies”**

- **The 3rd Law of Thermodynamics** serves to define the zero of the entropy scale. Several statements of this law have been proposed:

  - **Nernst (1906):** For any isothermal process \( \Delta S_T \to 0 \) as \( T \to 0 \).
  
  - **Nernst (1912):** The absolute zero of temperature is unattainable.
  
  - **Planck (1912):** The entropy of a chemically homogeneous solid or liquid substance has the value zero at the absolute zero of temperature.

We will adopt the definition offered in the textbook:

> Every substance has a finite positive entropy, but at zero Kelvin the entropy may become zero, and does so in the case of perfectly crystalline substances.

This last statement is in keeping with the statistical mechanical definition of entropy in terms of order – at 0 K systems in equilibrium should exist in their lowest energy quantum states, which should have a degeneracy \( \Omega \) of 1 (or at least of order 1).

- Adopting the convention \( S=0 \) at \( T=0 \) K defines the scale of “3rd Law” or “practical absolute entropies”. Given this convention the entropy at any temperature can be determined from an integration of heat capacity data of the form:

\[
\overline{S}^o(T) = \int_0^T \frac{C_p^o(T')}{T'} dT' + \frac{\Delta_{p=1}^o H^o}{T_{p=1}} + \cdots \int_{T_{ex}}^T \frac{\overline{C_p^o}(T')}{T'} dT'
\]

This expression incorporates integrations over \( \overline{C_p^o}(T) \) in regions where a single phase exists, as well as the discontinuous changes that occur at phase transitions

\[
\Delta_{p=1}^o S^o = \frac{\Delta_{p=1}^o H^o}{T_{p=1}}
\]

The superscripts “°” in these expressions denote standard state conditions \((P = 1 \text{ bar and the standard state of the compound of interest})\).

- The caveat “practical” applied to the entropies determined in this manner is a reminder that two sources of disorder / entropy are ignored in these 3rd-Law entropies – the entropy associated with nuclear spins and the entropy of isotopic mixing. Since nuclei are conserved in chemical processes, it is not necessary to account for either of these potential sources of disorder in thermochemical calculations (except perhaps in the case of \( \text{H}_2 \)).
Some representative $C_p(T)$ data and the resulting $S^*(T)$ data are plotted below:


---

### Low Temperature Heat Capacities

- It is important to understand the behavior of heat capacities as $T \to 0$ because it is always necessary to extrapolate available data to $T \to 0$ in order to calculate 3rd Law entropies.
- The 3rd Law requirement that $S \to 0$ as $T \to 0$ (or at least that $S$ remain finite) implies that $C_p \to 0$ as $T \to 0$.
- Statistical mechanical models for the behavior of solids at low temperature provide useful relations for the limiting low-temperature dependence of $C_p(T)$. For example, the **Debye theory** (1912) is an extension of the Einstein model discussed previously. It provides the correct limiting behavior of the **heat capacity due to crystal lattice vibrations** for most non-crystalline nonmetallic crystals. The predictions of the Debye model can be summarized:

$$\frac{C_v(T)}{R} = g \left( \frac{T}{\Theta_D} \right)^3 \frac{e^u u^4 du}{(e^u - 1)^3}$$

where $\Theta_D$ is the “Debye temperature”, a characteristic of a given solid, which is usually treated as an empirical constant. Examples of fits of experimental data to this functional form are illustrated below.
The limiting behavior predicted by the Debye theory is:

\[
\frac{\bar{C}_v}{R} \rightarrow \frac{12\pi^4}{5\Theta^3_D} T^3 \quad \text{for} \quad (T/\Theta_D) \ll 1 \quad \text{and} \quad \frac{\bar{C}_v}{R} \rightarrow 3 \quad \text{for} \quad (T/\Theta_D) \gg 1
\]

- Note the scaling of \( T \) by a single characteristic parameter \( \Theta_D \). This scaling implies that \( \bar{C}_v(T/\Theta_D) \) is a universal function for all solids that fit the Debye model. This corresponding states behavior is indeed observed for monatomic solids, but not for solids of more complicated molecules or ions. However, the limiting \( T^3 \) dependence as \( T \to 0 \) is general.

- At low enough temperatures other mechanisms of energy storage may become important. One such mechanism is the electronic heat capacity due to valence electrons in a metal. The contribution of this mechanism can be calculated using an electron gas model. The result is:

\[
\frac{\bar{C}_v(\text{el})}{R} = n \pi^2 \left( \frac{T}{T_F} \right)
\]

where \( n \) is the number of valence electrons and \( T_F \) is the Fermi temperature \( (\varepsilon_F/k_B \text{ where } \varepsilon_F \text{ is the energy of the highest occupied state at } 0 \text{ K}; T_F \sim 10^4 \text{ K} \text{ is typical}) \). The relative magnitudes of electronic and lattice vibrational heat capacities for two simple metals are tabulated below:

**Electronic Heat Capacity in Typical Metals**

<table>
<thead>
<tr>
<th>Solid</th>
<th>( T_F ) (/(10^4 \text{ K}) )</th>
<th>( \frac{A_{\text{obs}}}{A_{\text{calc}}} )</th>
<th>( \frac{C_V(\text{el})}{10^{-4} \text{ R}} )</th>
<th>( \frac{C_V(\text{el})}{C_V(\text{tot})} )</th>
<th>( \frac{C_V(\text{el})}{10^{-4} \text{ R}} )</th>
<th>( \frac{C_V(\text{el})}{C_V(\text{tot})} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>8.2</td>
<td>1.3</td>
<td>1.8</td>
<td>0.78</td>
<td>27</td>
<td>0.013</td>
</tr>
<tr>
<td>Al</td>
<td>13.6</td>
<td>1.4</td>
<td>3.5</td>
<td>0.92</td>
<td>52</td>
<td>0.0051</td>
</tr>
</tbody>
</table>

• In light of these two mechanisms, the limiting low-temperature behavior of crystals is usually:

\[ \overline{C}_p^o \approx \overline{C}_V^o \rightarrow aT^3 + bT \quad \text{as} \quad T \rightarrow 0 \]

\[ \overline{S}^o(T) \rightarrow \frac{a}{3}T^3 + bT \quad \text{as} \quad T \rightarrow 0 \]

• For non-metals the \( T^1 \) term is absent, and the entropy is simply related to the observed heat capacity:

\[ \overline{S}^o(T) \rightarrow \frac{1}{3}\overline{C}_p^o(T) \quad \text{as} \quad T \rightarrow 0. \]

3rd-Law integrations therefore often start with the value \( \overline{S}^o(T_{\text{min}}) = \frac{1}{3}\overline{C}_p^o(T_{\text{min}}) \) for the lowest temperature measured.

---

### Statistical Mechanical Calculation of the Entropies of Ideal Gases

• The machinery developed in Chapters 3 & 4 provides the means for calculating the entropies of ideal gases based on molecular constants obtained from spectroscopic measurements.

• Recall that the relation between \( S \), the total system partition function \( Q(N,V,T) \), and the molecular partition function \( q(V,T) \) (where \( Q(N,V,T) = q(V,T)^N / N! \)) can be written:

\[
S = k_B \ln Q + k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} = Nk_B \ln q - k_B \ln N! + Nk_B T \left( \frac{\partial \ln q}{\partial T} \right)_{N,V}
\]

Using Sterling’s approximation, \( \ln N! \approx N \ln N - N \), and choosing \( N=N_A \), this equation becomes:

\[
\overline{S} / R = 1 + \ln \left( \frac{q}{N_A} \right) + T \left( \frac{\partial \ln q}{\partial T} \right)_{N,V}
\]

The molecular partition function can be written \( q(V,T) = q_{\text{trans}}(V,T)q_{\text{rot}}(T)q_{\text{vib}}(T)q_{\text{el}}(T) \) where the individual pieces were described in “Topics 3&4”:

\[
q_{\text{trans}}(V,T) = \left( \frac{2\pi M k_B T a^2}{\hbar^2} \right)^{3/2} = \frac{V}{\Lambda^3}
\]

\[
q_{\text{rot}}(T) \approx \frac{1}{\sigma} \left( \frac{T}{\Theta_{\text{rot}}} \right)
\]

(linear molecules)

\[
q_{\text{rot}}(T) \approx \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_{\text{rot}}^4 \Theta_{\text{rot}}^B} \right)^{1/2}
\]

(nonlinear molecules)

\[
q_{\text{vib}}(T) = \prod_{i=1}^{f_{\text{vb}}} q_{\text{ho}}^{(i)} = \prod_{i=1}^{f_{\text{vb}}} \frac{e^{-\Theta_{\text{vib}}^{(i)}/T}}{1 - e^{-\Theta_{\text{vib}}^{(i)}/T}}
\]

• As a result of this factorization, the entropy of an ideal gas, just like the energy, is a sum of translational, rotational, vibrational, and electronic contributions:
For linear molecules:

\[
\frac{\bar{S}}{R} = \ln \left( \frac{\sqrt{\pi e^{5/2}}}{\lambda^3 N_A} \right) + \ln \left( \frac{Te}{\sigma \Theta_{\text{rot}}} \right) + \sum_{i=1}^{3N-5} \left( \frac{\Theta_{vib}^i}{T} - \ln \left( 1 - e^{-\Theta_{vib}^i/T} \right) \right) + \ln g_{\text{el}}
\]

and for nonlinear molecules:

\[
\frac{\bar{S}}{R} = \ln \left( \frac{\sqrt{\pi e^{5/2}}}{\lambda^3 N_A} \right) + \ln \left( \left( \frac{\pi^{1/2}}{\sigma} \right)^{3/2} \left( \frac{T^4 \Theta_{\text{rot}} \Theta_{\text{vib}} \Theta_{\text{el}}}{\Theta_{\text{rot}}^2 \Theta_{\text{rot}}^2 \Theta_{\text{el}}^2} \right)^{1/2} \right) + \sum_{i=1}^{3N-6} \left( \frac{\Theta_{vib}^i}{e^{\Theta_{vib}^i/T} - 1} - \ln \left( 1 - e^{-\Theta_{vib}^i/T} \right) \right) + \ln g_{\text{el}}
\]

- Gas-phase entropies calculated in this way can be compared with practical absolute entropies, derived from integration of calorimetric data assuming \( T = 0 \) K. In most cases the two methods agree to within experimental uncertainties. Some comparisons are provided below.

<table>
<thead>
<tr>
<th>Gas</th>
<th>( S_{\text{cal}} )</th>
<th>( S_{\text{stat}} )</th>
<th>( S_{\text{cal}} )</th>
<th>( S_{\text{stat}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>35.01</td>
<td>34.95</td>
<td>51.11</td>
<td>51.07</td>
</tr>
<tr>
<td>Ar</td>
<td>36.95</td>
<td>36.99</td>
<td>59.24</td>
<td>59.27</td>
</tr>
<tr>
<td>Kr</td>
<td>39.17</td>
<td>39.20</td>
<td>67.81</td>
<td>67.81</td>
</tr>
<tr>
<td>Xe</td>
<td>40.7 (± 0.3)</td>
<td>40.54</td>
<td>45.94</td>
<td>45.91</td>
</tr>
<tr>
<td>Cd</td>
<td>40.0</td>
<td>40.1</td>
<td>50.35</td>
<td>50.37</td>
</tr>
<tr>
<td>Zn</td>
<td>38.4</td>
<td>38.5</td>
<td>53.15</td>
<td>53.18</td>
</tr>
<tr>
<td>Hg</td>
<td>41.3 (± 0.6)</td>
<td>41.8</td>
<td>55.94</td>
<td>55.98</td>
</tr>
<tr>
<td>N₂</td>
<td>45.9</td>
<td>45.79</td>
<td>57.9</td>
<td>58.0</td>
</tr>
<tr>
<td>O₂</td>
<td>49.09</td>
<td>49.03</td>
<td>65.73</td>
<td>65.73</td>
</tr>
<tr>
<td>Cl₂</td>
<td>53.32</td>
<td>53.31</td>
<td>52.48</td>
<td>52.47</td>
</tr>
<tr>
<td>HCl</td>
<td>44.5</td>
<td>44.64</td>
<td>54.17</td>
<td>54.26</td>
</tr>
<tr>
<td>HBr</td>
<td>47.6</td>
<td>47.53</td>
<td>64.46</td>
<td>64.36</td>
</tr>
<tr>
<td>HI</td>
<td>49.5</td>
<td>49.4</td>
<td>76.77</td>
<td>76.68</td>
</tr>
<tr>
<td>H₂S</td>
<td>49.1</td>
<td>49.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Comparison of \( S_{\text{cal}} \) and \( S_{\text{stat}} \) for Gases (\( T = 298.15 \) K Unless Otherwise Noted and Entropies Are in Calories per Kelvin per mole)

<table>
<thead>
<tr>
<th>Gas</th>
<th>( T/K )</th>
<th>( S_{\text{cal}} )</th>
<th>( S_{\text{stat}} )</th>
<th>( S_{\text{cal}} - S_{\text{stat}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>298.15</td>
<td>46.2</td>
<td>47.31</td>
<td>1.1</td>
</tr>
<tr>
<td>N₂O</td>
<td>298.15</td>
<td>51.4</td>
<td>52.58</td>
<td>1.2</td>
</tr>
<tr>
<td>NO</td>
<td>298.15</td>
<td>49.7</td>
<td>50.43</td>
<td>0.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>298.15</td>
<td>44.28</td>
<td>45.104</td>
<td>0.82</td>
</tr>
<tr>
<td>D₂O</td>
<td>298.15</td>
<td>45.89</td>
<td>46.66</td>
<td>0.77</td>
</tr>
<tr>
<td>H₂C═CD₂</td>
<td>169.40</td>
<td>48.48</td>
<td>49.84</td>
<td>1.36</td>
</tr>
<tr>
<td>CH₃D</td>
<td>99.7</td>
<td>36.72</td>
<td>39.49</td>
<td>2.77</td>
</tr>
<tr>
<td>H₂</td>
<td>298.15</td>
<td>29.74</td>
<td>31.208</td>
<td>1.47</td>
</tr>
<tr>
<td>D₂</td>
<td>298.15</td>
<td>33.9</td>
<td>34.62</td>
<td>0.7</td>
</tr>
</tbody>
</table>

When activation barriers prevent complete relaxation, “frozen-in” configurational entropy can persist in the solid state down to 0 K. In such cases \( S^\circ (0 \text{ K}) \neq 0 \) and as a result the entropy deduced from calorimetric measurements at higher temperatures is less than that obtained from calculations (or other means). Most instances of frozen-in entropy are found in glass-forming substances and in crystals of quasi-symmetric molecules which can adopt nearly equivalent orientations in the solid state. Examples in the latter category are also illustrated in part (b) of the previous tabulation.

### Entropies of Reaction \( \Delta_s S^\circ \)

- The **standard entropy of reaction**, \( \Delta_s S^\circ (T) \), is the entropy associated with complete conversion of reactants to products of a molar quantity of the reaction (as written). All species are in pure form at the standard pressure of 1 bar and at some specified temperature \( T \). Denoting a chemical reaction by \( \sum_i \nu_i A_i = 0 \), the standard entropy of reaction can be calculated from practical absolute entropies via:

\[
\Delta_s S^\circ (T) = \sum_i \nu_i S_i^\circ (T)
\]

### Interpreting and Estimating the Magnitudes of \( S^\circ \) and \( \Delta_s S^\circ \)

- Entropy is a direct measure of the number of states available to a system via \( \Omega = \exp(S^\circ / R) \).

- A few generalizations concerning the magnitude of \( S^\circ / R \) are:
  - The **entropies of solids** conforming to the Debye model can be estimated at temperatures greater than \( \Theta_D \) from the equation:
    \[
    S / R \approx 3 \ln(T / \Theta_D) + 4
    \]
  - The **entropies of fusion** of monatomic solids are usually in the range of 1.0\( R \) to 1.7\( R \). (Rare gases have values near 1.7\( R \); most metals have values nearer to 1.3\( R \).) Lattices composed of single ions behave as monatomic solids with entropies of fusion in the range 1.2\( R \) – 1.7\( R \) per ion. Molecular substances of similar structure have approximately equal values of the sum of the entropies of fusion and any solid-solid transitions that may exist.
  - The **entropies of vaporization** at the boiling temperature of a liquid and 1 bar pressure are close to 10.5\( R \) for most non-associated substances. This observation is known as “Trouton’s rule” (formulated in 1884).

- The entropies of **isomeric sets of molecules** can often be ranked according to the nature of the bonding present. Entropy increases with flexibility. Cyclic and branched structures tend to reduce the number of configurations accessible to a molecule and these bonding patterns therefore reduce the value of \( S^\circ / R \).

- Since the entropies of gases are typically much larger than the entropies of condensed phases under standard conditions, the sign and approximate magnitude of reaction entropies are often determined by the change in the numbers of gas-phase species in reaction.