A. Work and the Second Law of Thermodynamics

One of the most important consequences of the Second Law is the limitation it places on the efficiency with which an energy transformation can produce useful work.

- **Question.** What is a condition required for the production of work?
  
  **Answer.** A thermal gradient, a gradient in the electrical potential, a gravitational potential that causes a mass to fall, etc. When these conditions exist, useful work may be produced.

- The flow of energy in the biological work is initiated by radiant energy from the sun, which enables photosynthesis, which in turn produces carbohydrates. The respiratory systems of animals utilize oxygen, carbohydrates and other foodstuffs to produce biologically useful work…and lots of entropy. How efficient is the production of useful work in the biological world and in general?

Consider a simple work production scheme. An “engine” (i.e. the system) exploits a thermal gradient in the surroundings…consisting of a heat reservoir at a high temperature $T_h$ and a low temperature reservoir at $T_l$. See diagrams below…

- If the two heat reservoirs are brought into direct contact (left, above) a quantity of heat $q$ is transferred from the high temperature reservoir to the low temperature reservoir. Because the temperatures $T_h$ and $T_l$ are very, very different the heat transfer is irreversible and the entropy change is $\Delta S = q \left( \frac{1}{T_l} - \frac{1}{T_h} \right) > 0$. No work is produced by this process.

- Suppose the two reservoirs are not allowed to come into direct contact. Instead, an engine transfers heat $q_h$, *reversibly* (see text Example 3-2 and problem 3.9) from the
high temperature reservoir. The engine converts some of the heat to work and exhausts the remaining heat $q_l$ to the low temperature reservoir.

- **Question:** How efficient can an “engine” be in accomplishing the conversion of “useless” heat energy into “useful” work energy? Specifically, can all the heat $q_h$ be converted to work with no exhaust heat $q_l$ occurring at all? To answer this question a design for the “engine” must be proposed and tested.

Most man-made engines are cyclic devices. This means at the end of a work cycle the moving parts of the engine are restored to their original thermodynamic states...ready to work again. A piston in a car is a good example. After firing, hot gases in the piston cylinder of a car increase their volume pushing the piston outward. But at the end of the cycle the piston must be restored to its original thermodynamic state to the work cycle can be repeated. Consider a 4-step work cycle, shown below in several forms...

The engine consists of an ideal gas is confined to a cylinder by a frictionless piston. The ideal gas is placed in thermal contact with the high temperature reservoir and heat $q_h$ is transferred *reversibly* at temperature $T_h$ to the gas from the reservoir.

- **Step 1:** The engine is designed so the first step of the cycle is an isothermal expansion, $T=T_h$ from $V_1$ to $V_2$. The work done is $w_{\text{Step 1}} = -nR_T \ln \left( \frac{V_2}{V_1} \right)$ with an entropy change

$$
\Delta S_{1 \to 2} = \frac{q_h}{T_h}.
$$

- **Step 2:** The engine is designed to continue the reversible expansion from $V_2$ to $V_3$, but to do so *adiabatically*. This means no further heat is absorbed from the reservoir. Because the engine is doing work as the gas expands, the energy of the gas must decrease and because the gas is ideal this means the temperature must decrease to $T_l$. Because the process is reversible the entropy change for step 2 is

$$
\Delta S_{2 \to 3} = \int_{2}^{3} \frac{dq_{\text{rev}}}{T} = 0
$$
• Step 3: The engine now reverses the piston movement. The piston compresses the gas isothermally and reversibly from $V_3$ to $V_4$, giving off heat $q_l$ at $T=T_l$. The entropy change is $\Delta S_{3\rightarrow4} = \frac{q_l}{T_l}$.

• Step 4 is a adiabatic, reversible compression from $V_4$ back to $V_1$. Because work is done in compressing the gas with the piston, the temperature of the gas must increase from $T_l$ back to $T_h$. The system, i.e. the gas in the cylinder and the piston, is restored to its original state. Because this step is adiabatic and reversible the entropy change for this step, like step 2, is zero i.e. $\Delta S_{4\rightarrow1} = 0$

Comments:
• Because the change is cyclic, the system begins and ends at state, all state function changes are zero for the entire cycle.
  • For the entropy this means $\Delta S_{\text{cycle}} = \Delta S_{1\rightarrow2} + \Delta S_{2\rightarrow3} + \Delta S_{3\rightarrow4} + \Delta S_{4\rightarrow1} = 0$

Substituting...$\Delta S_{\text{cycle}} = \frac{q_h}{T_h} + 0 + \frac{q_l}{T_l} + 0 = \frac{q_h}{T_h} + \frac{q_l}{T_l} = 0$

• The work performed over the cycle $-w_{\text{cycle}}$ is equal to the difference between the magnitudes of the input heat $q_h$ and the exhausted heat $-q_l$...
  • $-w_{\text{cycle}} = q_h - (-q_l) = q_h + q_l$

• The efficiency of this process is the amount of work divided by the amount of heat adsorbed...$\text{efficiency} = \frac{-w_{\text{cycle}}}{q_h} = \frac{q_h + q_l}{q_h}$

• The result for the entropy change for the cycle $\frac{q_h}{T_h} + \frac{q_l}{T_l} = 0$ ⇒ $q_l = -q_h \frac{T_l}{T_h}$ can be used to eliminate $q_l$ from the efficiency

$\text{efficiency} = \frac{-w_{\text{cycle}}}{q_h} = \frac{q_h + q_l}{q_h} = \frac{q_h - q_h \frac{T_l}{T_h}}{q_h} = \frac{T_h - T_l}{T_h}$

This equation i.e. $\text{efficiency} = \frac{-w_{\text{cycle}}}{q_h} = \frac{T_h - T_l}{T_h}$ means that work can only be produced with limited efficiency...which is limited by the size of the thermal gradient 100% efficiency in work production can only be achieved if $T_l=0K$...a condition which is not achievable in any practical sense.

B. Third Law of Thermodynamics

The equation of Boltzmann states that the absolute entropy $S$ can be related to the number of microstates in the macroscopic state $W$. $S = k_B \ln W$. $W$ is sometimes called the degeneracy of the system. In thermodynamic processes, only changes in state function $\Delta E$, $\Delta H$, $\Delta S$, etc. are calculated, but the equation of Boltzmann provides a means to obtain absolute entropies experimentally. The means to do this is summarized as the Third Law of Thermodynamics:
• The entropy of any pure substance (element or compound) in its equilibrium state approaches zero at an absolute temperature of zero (i.e. T=0K).

• The basic explanation of this Law is given by the equation \( S = k_B \ln W \) and the concepts discussed in Chapter 3 and Ch. 11. Lectures 1-3 in the Chemistry 355 page of the Drobny Web Site also deal with this issue more extensively. Temperature specifies the distribution of particles among the quantum mechanical states of a system. As the temperature increases more states become populated. But as the temperature approaches absolute zero i.e. \( T \to 0K \), the number of populated states decreases toward 1, i.e. \( W \to 1 \). At T=0K, where \( W=1 \), the absolute entropy \( S=k_B\ln(1)=S_0=0 \).

• The standard, absolute entropy at P=1 atm. and at a temperature T \( S^0(T) \) can be measured by beginning at T=0K where the absolute entropy \( S^0(0)=0 \) and calculating the increase of entropy with temperature using the expression \( \Delta S = n \int_{T_i}^{T_f} \frac{\bar{c}_p}{T} dT \) and when a phase transition is passed adding the entropy increase \( \Delta S = n \frac{\Delta H}{T} \), where \( \Delta H \) is the molar heat of the phase transition, and T is the temperature of the phase transition. In general:

\[
\frac{S^0(T)}{n} = \int_0^{T_{fusion}} \frac{\bar{c}_p (solid)}{T} dT + \frac{\Delta H_{fusion}}{T_{fusion}} + \int_{T_{fusion}}^{T_{exp}} \frac{\bar{c}_p (liquid)}{T} dT + \frac{\Delta H_{vap}}{T_{vap}} + \int_{T_{vap}}^T \frac{\bar{c}_p (vapor)}{T} dT
\]

Example: For the chemical reaction \( N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \)
Using the data in appendix 1 to calculate the entropy change of the system, surroundings, and the entropy change for the universe. Is the direction of the reaction as shown the spontaneous direction for the reaction at T=298K,

a) Entropy of system
\[
S^0(N_2(g)) = 191.50 J/mole \cdot K \\
S^0(O_2(g)) = 205.03 J/mole \cdot K \\
S^0(NO_2(g)) = 239.95 J/mole \cdot K
\]
\[
\Delta S^0 = 2S^0(NO_2(g)) - 2S^0(O_2(g)) - S^0(N_2(g))
\]
\[
= 2(239.95 J/mole \cdot K) - 2(205.03 J/mole \cdot K) - 191.50 J/mole \cdot K = -121.66 J/K
\]

b) Entropy of surroundings. This can be calculated by assuming the heat of the reaction is exchanged with the surroundings at T=298K. The heat of the reaction can be calculated from standard enthalpies of formation...also found in appendices in our text and other texts...
\[ \Delta H^0 = 2\left(\Delta H^0_\text{r} \left(NO_2(g)\right)\right) - 2\left(\Delta H^0_\text{r} \left(O_2(g)\right)\right) - \Delta H^0_\text{r} \left(N_2(g)\right) \]
\[ = 2(33,850 J/mole) - 2(0) - 0 = 67,700 J \]
\[ \therefore \Delta H_{\text{surr}} = -67,700 J \]
\[ \Delta S_{\text{surr}} = -\frac{67,700 J}{298 K} = -227.2 J/K \]

The entropy change of the universe is obtained by summing the results from parts a and b... \[ \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} = (−121.7 − 227.2) J/K = −348.9 J/K \]

The negative entropy change for the universe indicates that the direction written for the reaction is not the spontaneous direction at T=298K.

**Trends in Absolute Molar Entropies**

The following trends in tabulated molar entropies may be noted:

- A common observation is that entropy is related to hardness.
  - Hard gem-like solids like diamond, topaz, quartz, fused zirconium, etc. have small molar entropies while softer solids like lead have larger entropies.
    - Diamond \( S^0 = 2.37 \text{ J/mole-K} \)
    - Platinum \( S^0 = 41.63 \text{ J/mole-K} \)
    - Lead \( S^0 = 64.81 \text{ J/mole-K} \)
- Complex substances have higher molar entropies than simpler substances of similar hardness.
  - NaCl (s) \( S^0 = 72.13 \text{ J/mole-K} \)
  - ZnCl2 (s) \( S^0 = 111.46 \text{ J/mole-K} \)
- Melting and vaporization always lead to large changes in the molar entropy
  - \( H_2O \text{ (s)} S^0 = 40.96 \text{ J/mole-K} \)
  - \( H_2O \text{ (l)} S^0 = 63.12 \text{ J/mole-K} \)
  - \( H_2O \text{ (g)} S^0 = 185.6 \text{ J/mole-K} \)
- Molar entropy for particular motions can be correlated the heat capacity of that motion which in turn indicates the ease with which a substance absorbs heat for this motion at a given temperature. The more readily a substance absorbs heat for a given motion the higher is its heat capacity and the higher is the contribution of that motion to the molar entropy. The absorption of heat may in turn be correlated with the quantization which will be treated in Chemistry 453.
- For water vapor at 298K with 9 degrees of freedom:
  \[
  \begin{array}{cccc}
  S^0_{\text{(total)}} & S^0_{\text{translational}} & S^0_{\text{rotational}} & S^0_{\text{vibrational}} \\
  188.7 \text{ J/mole-K} & 144.6 \text{ J/mole-K} & 43.9 \text{ J/mole-K} & <1 \text{ J/mole-K}
  \end{array}
  \]
  Electronic motions have virtually no contribution to the molar entropy.