Entropy Changes & Processes

Chapter 4 of Atkins: The Second Law: The Concepts
Section 4.4 - 4.7

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The Third Law of Thermodynamics

At absolute zero, or when \( T = 0 \) K, all energy of thermal motion has been quenched, and all atoms or ions in a perfect crystalline lattice are in a perfect continuous array:

- No spatial disorder
- No thermal motion
- Entropy is zero; if \( S = 0 \), there is only one way of arranging the molecules

Cannot actually reach absolute zero - everything has some internal energy!

What good is the Third Law? It allows us to realize that as \( T \) approaches zero, the absolute entropy tends towards zero. The effects of the third law are most keenly felt at very low temperatures (not everyday stuff).

The third law also lets us define some entropies of substances relative to their perfect crystals at 0 K. Useful bookkeeping device!

Nernst Heat Theorem

The entropy change accompanying a physical or chemical transformation approaches zero as \( T \) approaches zero:

\[
S \to 0 \quad \text{as} \quad T \to 0
\]

Consider transition from orthorhombic sulfur \( S(\alpha) \) to monoclinic sulfur \( S(\beta) \) in the solid state. At the transition \( T \) (369 K):

\[
\Delta S = S(\alpha) - S(\beta) = \frac{-402 \text{ J mol}^{-1}}{369 \text{ K}} = -1.09 \text{ J mol}^{-1} \text{ K}^{-1}
\]

Two entropies can be determined from measuring heat capacities from \( T = 0 \) K to \( T = 369 \) K:

\[
S_\alpha(\alpha) = S_\alpha(\alpha,0) + 37 \text{ J mol}^{-1} \text{ K}^{-1} \quad S_\beta(\beta) = S_\beta(\beta,0) + 38 \text{ J mol}^{-1} \text{ K}^{-1}
\]

So at the transition temperature:

\[
\Delta S = S_\alpha(\alpha,0) - S_\beta(\beta,0) = 1 \text{ J mol}^{-1} \text{ K}^{-1}
\]

Third Law & The Nernst Heat Theorem

If we decide to assign a value zero to entropies of elements in their perfect crystalline form at \( T = 0 \), then all perfect crystalline compounds have entropy \( S = 0 \) at \( T = 0 \)

Third Law of Thermodynamics

If the entropy of every element in its most stable state at \( T = 0 \) is taken as zero, then every substance has a positive entropy which at \( T = 0 \) may become zero, which is also zero for all perfect crystalline substances, including compounds

This does not mean that the entropy at \( T = 0 \) is really zero: it means that all perfect crystalline substances have the same entropy at that temperature (choosing the value \( S = 0 \) at this temperature is a convention, and as mentioned, leads to some very neat bookkeeping for comparing relative entropies)
**Third Law Entropies**

The choice \( S(0) = 0 \) for perfect crystals is made from now on, and entropies reported relative to this value are called **Third Law Entropies** (or just **standard entropies**)

A substance in its standard state at temperature \( T \) has a standard entropy which is denoted as \( S^\varphi(T) \)

**Standard reaction entropies** are defined as

\[
\Delta S^\varphi = \sum_j n_j S^\varphi_j(T)
\]

and are weighted by stoichiometric coefficients in the same way that enthalpies are weighted

**Example:** Calculate \( \Delta S^\varphi \) of \( \text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)} \) at 25°C

\[
\Delta S^\varphi = \sum_j n_j S^\varphi_j(T) = \{ -112.1 \text{ J K}^{-1} \text{ mol}^{-1} \} - 33.15 \text{ J K}^{-1} \text{ mol}^{-1} + 99.6 \text{ J K}^{-1} \text{ mol}^{-1} = -21.0 \text{ J K}^{-1} \text{ mol}^{-1}
\]

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**Reaching Low Temperatures**

Temperatures below 4 K (the boiling point of He) can be achieved by evaporating He through large radius pipes (down to 1 K) by Joule-Thomson expansion

Lower temperatures (down to 20 nK) can be achieved by **adiabatic demagnetization** - without a magnetic field, \( \text{e}^- \) in **paramagnetic materials** are oriented randomly; however, in the presence of a magnetic field, the **spin** of the \( \text{e}^- \) comes into play

There are more \( \alpha \) spins (+1/2) than \( \beta \) spins (-1/2), and the entropy of the sample is lowered (the spins are **biased** to point one way or the other)

Paramagnetic substances are cooled to 1 K with liquid He, and then the application of a magnetic field lowers the energy of the unpaired electrons isothermally (step \( A \rightarrow B \))

The spins are in a lower energy state, He is pumped off, the magnetic field removed and thermal contact is broken (adiabatic demagnetization, step \( B \rightarrow C \)). The sample is the same as at \( A \), except with lower entropy and \( T \).

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**2001 Nobel Prize in Physics: BEC**

Eric A. Cornell (NIST), Wolfgang Ketterle (MIT) & Carl E. Wieman (University of Colorado)

"for the achievement of Bose-Einstein condensation in dilute gases of alkali atoms, and for early fundamental studies of the properties of the condensates"

In 1924 the Indian physicist Bose made important theoretical calculations regarding light particles. Einstein predicted that if a gas of such atoms were cooled to a very low temperature all the atoms would suddenly gather in the lowest possible energy state. Seventy years were to pass before these Nobel Laureates, in 1995, succeeded in achieving this extreme state of matter. Cornell and Wieman then produced a pure condensate of about 2 000 rubidium atoms at 20 nK (nanokelvin), i.e. 0.000 000 02 degrees above absolute zero.

Independently of the work of Cornell and Wieman, Ketterle performed corresponding experiments with sodium atoms.

Please visit: http://www.nobel.se to see more about this year's prizes, esp. the prize for the development of MRI.
Helmholtz and Gibbs Energies

We will now focus almost exclusively on entropy changes within the system (treating the surroundings and total entropy is trivial)

Consider a system in thermal equilibrium with surroundings, at temperature $T$. For a change in the system with transfer of heat, the Clausius inequality is:

\[\text{Heat transfer at constant V} \quad dS - \frac{dq}{T} \geq 0 \quad \text{Heat transfer at constant p} \quad dS - \frac{dH}{T} \geq 0\]

(no non-expansion work)

In both cases, criteria for spontaneous change are expressed solely in terms of state functions. Below, subscripts indicate constant properties:

- Constant $dU = 0$ or $dS = 0$
- Constant $dH = 0$ or $dS = 0$

\[dS - \frac{dH}{T} \geq 0 \quad \text{and} \quad TdS \geq dH\]

To interpret these inequalities, consider the constant V cases:

1. The first inequality says that for a system at constant volume and constant internal energy (e.g., isothermal system), entropy increases in a spontaneous change
2. The second inequality says if $S$ and $V$ are constant, then internal energy must decrease with spontaneous change - system doesn’t spontaneously go to lower energy; rather, if $\Delta S_{sys} = 0$, then $\Delta S_{sur} > 0$, if energy flows out of system as heat, and system energy decreases.

Inequalities on previous slide reformed as $dU - TdS \leq 0$ and $dH - TdS \leq 0$,
we can write them as two new thermodynamic quantities:

- **Helmholtz Energy, $A$**
  \[A = U - TS\]
  \[\begin{align*}
  dA &= dU - TdS \\
  \Delta A &\leq 0
  \end{align*}\]

- **Gibbs Energy, $G$**
  \[G = H - TS\]
  \[\begin{align*}
  dG &= dH - TdS \\
  \Delta G &\leq 0
  \end{align*}\]

Helmholtz Energy is useful also for indicating the maximum amount of work accompanying a process (A called maximum work function)

\[\Delta w_{\text{max}} = dA\]

How do we prove this? Combine the Clausius inequality, $dS \geq dq/T$ in the form $TdS \geq dq$ with the first law $U = q + w$.

\[dU \leq TdS + dw\]

\[\Delta U = dU - TdS\]

$dU$ is smaller than the RHS b/c we replace $dq$ by $TdS$ (which is in general larger), and rearranging:

\[\Delta w_{\text{max}} = du - TdS\]

The most negative value of $\Delta w_{\text{max}}$ and therefore the maximum energy obtained from the system as work is

\[\Delta w_{\text{max}} = \Delta U - TdS\]

which only applies on a reversible path (hence the equality in the equation), and $\Delta w_{\text{max}} = dA$ at constant $T$. 

Helmholtz Energy change in a system at constant temperature and volume is spontaneous if $\Delta A_{sys} \leq 0$ (change under these conditions corresponds to decrease in $A$)

\[A = U - TS\]

\[\begin{align*}
  \Delta A &= dU - TdS \\
  \Delta A_{sys} &\leq 0
  \end{align*}\]

Equilibrium condition for complete reversibility, is when $\Delta A_{sys} = 0$

The above expressions can be interpreted as follows:

A negative $\Delta A$ is favored by negative $\Delta U$ and positive $T\Delta S$

Does system move to lower $A$ due to tendency to move towards states of lower internal energy and higher entropy? No, tendency towards lower $A$ is solely from a move towards states of greater overall entropy

Systems change spontaneously if the total entropy of system and surroundings increase, not because system tends towards lower internal energy; $dS$ is change in system entropy, $-dU/T$ is the entropy change of surroundings (when $V$ constant), and their total tends to a maximum.
Maximum Work, 2

For macroscopic measurable change:

\[ w_{\text{max}} = \Delta A \text{ where } \Delta A = \Delta U - T \Delta S \]

Depending upon the sign of \( T \Delta S \), not all of \( \Delta U \) is available for work.

Helmholtz Free Energy. \( \Delta A \) is the part of change in internal energy that we are free to use for work.

Molecular Interpretation: \( A \) is total internal energy \( U \), less a chaotically stored contribution, \( T \Delta S \).

If \( T \Delta S < 0 \), the RHS is not as negative as \( \Delta U \) itself, so maximum work is less than \( \Delta U \). For change to be spontaneous, some energy must escape as heat to generate enough entropy in surroundings to overcome reduction in entropy in system (\( \Delta S_{\text{TOT}} < 0 \)).

If \( T \Delta S > 0 \), the RHS is more negative than \( \Delta U \) itself, so maximum work is more than \( \Delta U \). System is not isolated, and heat can flow in as work is done. Some reduction in \( S_{\text{sur}} \) occurs, yet overall \( \Delta S_{\text{TOT}} > 0 \).

Calculating Maximum Work

When 1.000 mol \( C_6H_{12}O_6 \) is burned at 25°C:

\[
C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O (l)
\]

calorimeter measurements give \( \Delta rU_o = -2808 \text{ kJ mol}^{-1} \) and \( \Delta rS_o = + 182.4 \text{ J K}^{-1} \text{ mol}^{-1} \) at 25°C. How much of the energy is extracted as (a) heat at constant pressure and (b) work?

(a) \( \Delta rS_o = 0 \), so \( \Delta rH = \Delta rU - T \Delta rS = -2808 \text{ kJ mol}^{-1} \). So at constant pressure, energy available as heat is \( q = -2808 \text{ kJ mol}^{-1} \).

(b) At \( T = 298 \text{ K} \), we can calculate \( \Delta rP \) as \( \Delta rP = \Delta rU - T \Delta rS = -2862 \text{ kJ mol}^{-1} \).

So what this means is that burning glucose in oxygen can be used to produce a maximum of 2862 kJ mol\(^{-1}\) of work.

The maximum energy available for work is greater than the change in internal energy of the system due to the positive entropy change in the system (generating small molecules from one big molecule) — the system therefore draws energy from the surroundings (reducing their entropy) for doing work.

Gibbs Energy

The Gibbs energy, or free energy, is more commonly used in chemistry because we are interested mainly in constant pressure changes as opposed to constant volume changes.

\[
G = H - TS
\]

\[
dG = dH - TdS
\]

\[
dG_{\text{rev}} \leq 0
\]

The inequality \( dG_{\text{rev}} \leq 0 \) tells us that at constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.

If \( G \) decreases as a reaction occurs, the conversion of reactants into products is spontaneous.

If \( G \) increases during a reaction, the reverse reaction is spontaneous.

The existence of spontaneous endothermic reactions can be explained with \( G \). If \( H \) increases (spontaneously higher enthalpy), so \( dH > 0 \). The \( dS \) of this spontaneous reaction is \( < 0 \); the entropy increase must be high enough that \( TdS \) is larger and positive, and outweighs \( dH \).
### Maximum Non-Expansion Work

Maximum non-expansion work, $w_{add,max}$, is given by change in Gibbs energy:

$$dw_{add,max} = \Delta G$$

Since $H = U + pV$ for a general change, then

$$dH = dq + dw + d(pV)$$

Remembering that $G = H - TS$, then if the change is reversible, $dw = dw_{rev}$ and $dq = dq_{rev} = T\, dS$. Thus for a reversible and isothermal process:

$$dG = dH - T\, dS = dq_{rev} + d(pV)$$

Work consists of expansion work, $dw_{rev} = -p\, dV$, and some other kind of work (e.g., electrical work pushing electrons through a circuit, work raising a column of fluid, etc.). The latter work is non-expansion work, $dw_{add}$:

$$dG = (-pdV + dw_{add}) + pdV + V\, dp$$

And, if work occurs at constant $p$, then $dG = dw_{add}$ because the process is reversible, work has its maximum value here!

### Calculating Maximum Non-Expansion Work

How much energy is available for sustaining muscular and nervous system activity from combustion of 1.00 mol of glucose under standard conditions at 37°C (temperature of blood)?

- $\Delta_{r}H^\circ = -2808$ kJ mol$^{-1}$
- $\Delta_{r}S^\circ = +182.4$ J K$^{-1}$mol$^{-1}$

The non-expansion work available from the combustion can be calculated from the standard Gibbs energy,

$$\Delta_{r}G^\circ = \Delta_{r}H^\circ - T\, \Delta_{r}S^\circ$$

For the combustion of glucose:

$$\Delta_{r}G^\circ = -2808 \text{ kJ mol}^{-1} - (310 \text{ K}) \times (182.4 \text{ J K}^{-1}\text{mol}^{-1}) = -2865 \text{ kJ mol}^{-1}$$

So, $w_{add,max} = -2865$ kJ mol$^{-1}$ for combustion of 1 mole of glucose molecules in blood, and the reaction can be used to do up to 2865 kJ mol$^{-1}$ of non-expansion work!

### Standard Molar Gibbs Energies

The non-expansion work available from the combustion can be calculated from the standard Gibbs energy, $\Delta_{r}G^\circ$.

$$\Delta_{r}G^\circ = \Delta_{r}H^\circ - T\, \Delta_{r}S^\circ$$

The standard Gibbs energy of formation, $\Delta_{f}G^\circ$, is the standard reaction Gibbs energy for the formation of a compound from its elements in their reference states – $\Delta_{r}G^\circ$ can be expressed in terms of $\Delta_{f}G^\circ$:

$$\Delta_{f}G^\circ = \sum_{i}v_{i}\Delta_{f}G^\circ(i)$$

$\Delta_{f}G^\circ = 0$ for elements in their reference states, since their formation is a null reaction (see table 4.4 Atkins 7th Edition, or CRC Handbook).

Calorimetry (for $\Delta_{r}H$ directly and $\Delta_{r}S$ via heat capacities) is one way of determining Gibbs energies - however, they can be determined as well from reaction equilibrium constants, electrochemical measurements and spectroscopic measurements...