
Entropy Changes & Processes

The Second Law: The Concepts

Sections 4.4 - 4.7, 7th ed.; Sections 3.3-3.6, 8th and 9th eds.

Third Law of Thermodynamics

Nernst Heat Theorem

Third-Law Entropies

Reaching Very Low Temperatures

Helmholtz and Gibbs Energies

Helmholtz Energy

Maximum Work

Gibbs Energy

Maximum Non-Expansion Work

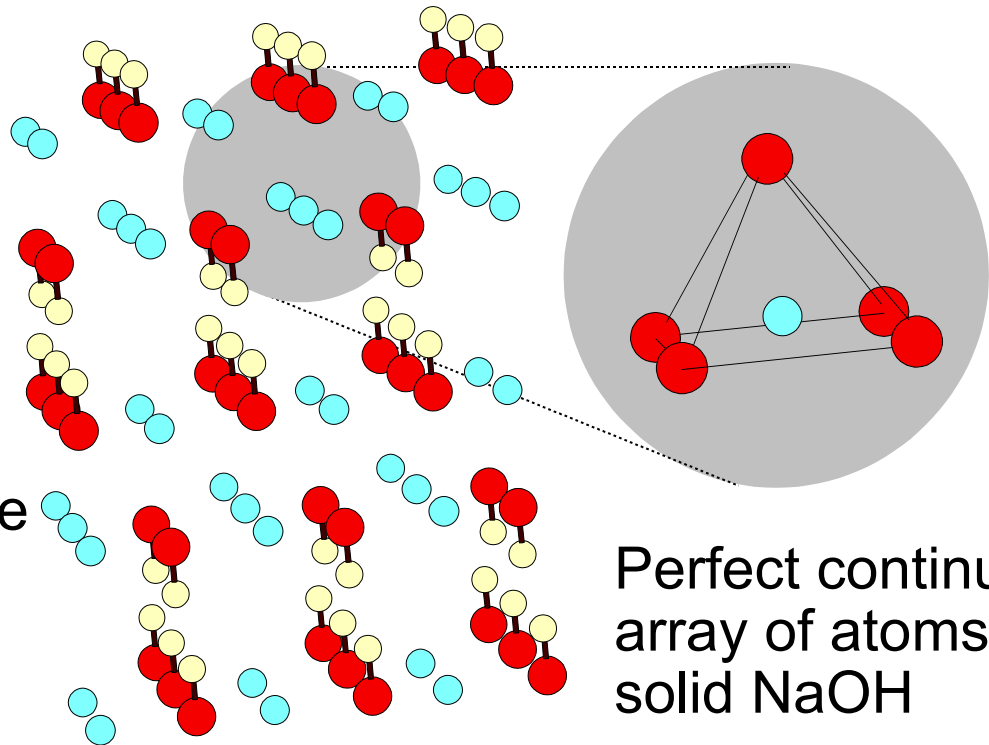
Standard Molar Gibbs Energies

Oct. 24, 2012: Slide 1 minor updates

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 book keeping device!

Nernst Heat Theorem

The entropy change accompanying a physical or chemical transformation approaches zero as the temperature approaches zero

$$\Delta S \rightarrow 0 \text{ as } T \rightarrow 0$$

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

$$\Delta_{\text{trs}} S = S_m(\alpha) - S_m(\beta) = \frac{(-402 \text{ J mol}^{-1})}{369 \text{ K}} = -1.09 \text{ J K}^{-1} \text{ mol}^{-1}$$

Two entropies can be determined from measuring heat capacities from $T = 0 \text{ K}$ to $T = 369 \text{ K}$:

$$S_m(\alpha) = S_m(\alpha, 0) + 37 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S_m(\beta) = S_m(\beta, 0) + 38 \text{ J K}^{-1} \text{ mol}^{-1}$$

So at the transition temperature:

$$\Delta_{\text{trs}} S = S_m(\alpha, 0) - S_m(\beta, 0) - 1 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S_m(\alpha, 0) - S_m(\beta, 0) \approx 0$$

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 = 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 $T = 0$** (choosing the value $S = 0$ at this temperature is a convenience, and as mentioned, leads to some very neat bookkeeping for comparing relative entropies)

Third Law Entropies

The choice $S(0) = 0$ for perfect crystal 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 $S^\circ(T)$

Standard reaction entropies are defined as

$$\Delta_r S^\circ = \sum_{\text{products}} \nu S_m^\circ - \sum_{\text{reactants}} \nu S_m^\circ = \sum_J \nu_J S_m^\circ(J)$$

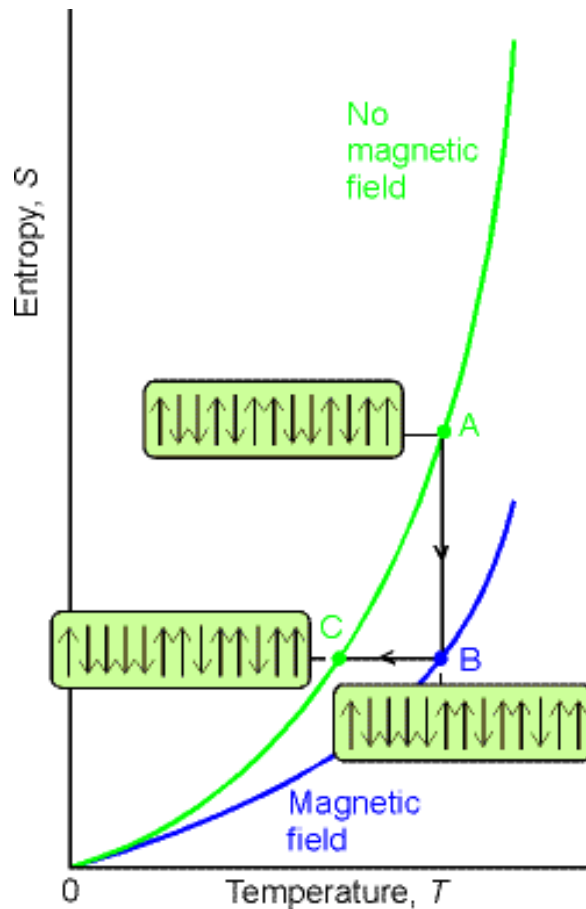
and are weighted by stoichiometric coefficients in the same way that enthalpies are weighted

Example: Calculate $\Delta_r S^\circ$ of $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ at 25°C

$$\begin{aligned}\Delta_r S^\circ &= S_m^\circ(\text{H}_2\text{O}, \text{l}) - S_m^\circ(\text{H}_2, \text{g}) - \frac{1}{2}S_m^\circ(\text{O}_2, \text{g}) \\ &= 69.9 - \{130.7 + \frac{1}{2}(205.0)\} \text{ J K}^{-1} \text{ mol}^{-1} = -163.3 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

ΔS is negative, since a reaction in the gas phase \rightarrow liquid phase

Reaching Low Temperatures



- Temperatures < 4 K (boiling point of He) can be achieved by evaporating He through large radius pipes (down to 1K) by Joule-Thomson expansion
- Lower temperatures (**under $10 \mu\text{K}$**) can be achieved by **adiabatic demagnetization** - without a magnetic field, e- in **paramagnetic materials** are oriented randomly; however, in the presence of a magnetic field, the **spin** of the e- comes into play
- There are more α spins ($+1/2$) than β 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 application of a magnetic field lowers the energy of the unpaired e- **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.

2001 Nobel Prize in Physics: BEC*



KUNGL.
VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

The Prize Winners for 2001



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 the 2001 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. **In 2000: 450 pK reached!**

Please visit: <http://www.nobel.se>

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 temp. T
For change in the system with transfer of heat, the Clausius inequality is:

$$dS - \frac{dq}{T} \geq 0$$

Heat transfer at **constant V**

$$dS - \frac{dU}{T} \geq 0$$

$$T dS \geq dU$$

(no non-expansion work)

Heat transfer at **constant p**

$$dS - \frac{dH}{T} \geq 0$$

$$T dS \geq dH$$

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

Constant $dU = 0$ or $dS = 0$:

$$dS_{U,V} \geq 0 \quad dU_{S,V} \leq 0$$

Constant $dH = 0$ or $dS = 0$:

$$dS_{H,p} \geq 0 \quad dH_{S,p} \leq 0$$

Helmholtz and Gibbs Energies, 2

To interpret these inequalities, consider the constant V cases:

$$(1) \quad dS_{U,V} \geq 0 \quad (2) \quad dU_{S,V} \leq 0$$

- (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 $\Delta S_{\text{sys}} = 0$, then $\Delta S_{\text{sur}} > 0$, 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

$$A = U - TS$$

$$dA = dU - TdS$$

$$dA_{T,V} \leq 0$$

at constant T

Gibbs Energy, G

$$G = H - TS$$

$$dG = dH - TdS$$

$$dG_{T,p} \leq 0$$

Criteria for Spontaneity

Criteria for spontaneity & equilibrium:

- (1) Is a reaction spontaneous?
- (2) When rxn reaches equilibrium, what is the ratio of products & reactants?

A. H and U : not satisfactory

Just because the energy of a system is lowered does not mean that this is automatically the direction of spontaneous progress.

Examples: many salts have negative $\Delta_{\text{soln}} H^\circ$; ice melts at 25 °C

- Both processes take heat from the surroundings!

If a process occurs under const. S and p , then and only then is ΔH a criterion of spontaneity and equilibrium (similar statement for S , V and ΔU). Processes are spontaneous under these rarely found experimental conditions iff:

$$\Delta H_{S,p} \leq 0 \quad \text{or} \quad \Delta U_{S,V} \leq 0$$

B. S not satisfactory

For an isolated system, $\Delta V = 0$ and $\Delta U = 0$, and $\Delta S > 0$ for spontaneous process

$$\Delta S_{U,V} \geq 0$$

However, this is inadequate for realistically defining spontaneity, since knowledge of ΔS_{sys} and ΔS_{sur} (the latter is more difficult) are required

Process or reaction with constant p and T or V and T would be the best!

Helmholtz Energy

Change in system at **constant temperature and volume** is spontaneous if $dA_{T,V} \leq 0$ (change under these conditions corresponds to decrease in A)

$$A = U - TS$$

$$dA = dU - T dS$$

$$dA_{T,V} \leq 0$$

Equilibrium condition for complete reversibility is when $dA_{T,V} = 0$

The above expressions can be interpreted as follows:

A negative dA is favoured by negative dU and positive TdS

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 the 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), their total tends to a maximum

Maximum Work

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

$$dw_{\max} = dA$$

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

$$dU \leq T dS + dw$$

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

$$dw \geq dU - T dS$$

The most negative value of dw , and therefore the maximum energy obtained from the system as work is

$$dw_{\max} = dU - T dS$$

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

Maximum Work, 2

For macroscopic measurable change, where $\Delta U < 0$:

$$w_{\max} = \Delta A \quad \text{where} \quad \Delta A = \Delta U - T\Delta S$$

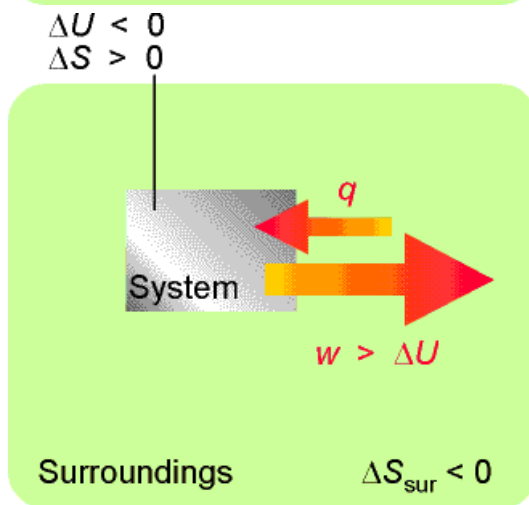
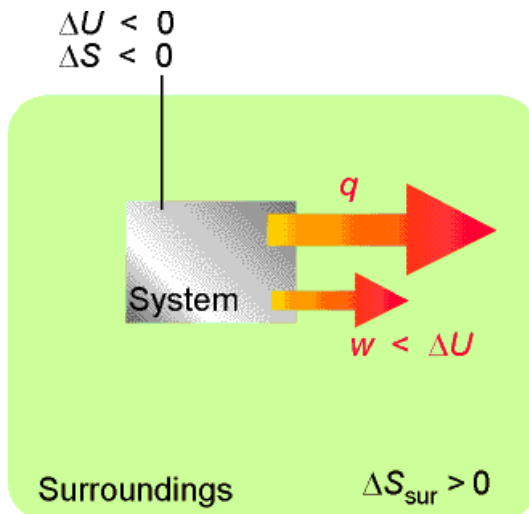
Depending upon the sign of $T\Delta S$, not all of ΔU is available for work

Helmholtz Free Energy, ΔA 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 $T\Delta S$

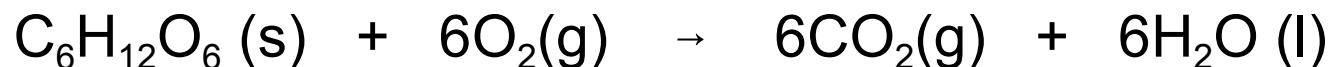
If $T\Delta S < 0$, the RHS is not as negative as ΔU itself, so maximum work is less than $|\Delta U|$. For change to be spontaneous, some energy must escape as heat to generate enough entropy in surroundings to overcome reduction in entropy in system ($\Delta S_{\text{TOT}} > 0$)

If $T\Delta S > 0$, the RHS is more negative than ΔU 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_{sur} occurs, yet overall $\Delta S_{\text{TOT}} > 0$



Calculating Maximum Work

When 1.000 mol $\text{C}_6\text{H}_{12}\text{O}_6$ is burned at 25°C :



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

(a) $\Delta n_g = 0$, so $\Delta_r U^\circ = \Delta_r H^\circ = -2808 \text{ kJ mol}^{-1}$. So at constant pressure, energy available as heat is $q = -2808 \text{ kJ mol}^{-1}$

(b) At $T = 298 \text{ K}$, we can calculate $\Delta_r A^\circ$ as

$$\Delta_r A^\circ = \Delta_r U^\circ - T\Delta_r S^\circ = -2862 \text{ kJ mol}^{-1}$$

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 the entropy of the surroundings) 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

$$G = H - TS$$

$$dG = dH - T dS$$

$$dG_{T,p} \leq 0$$

The inequality $dG_{T,p} \leq 0$ 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 : H increases (spontaneously higher enthalpy), so $dH > 0$. The dG 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_e , is given by change in Gibbs energy

$$dw_{e,\max} = dG, \quad w_{e,\max} = \Delta G$$

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

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

If change is reversible, $dw = dw_{\text{rev}}$, $dq = dq_{\text{rev}} = T dS$, $dG = dH - T dS$, thus

$$dG = TdS + dw_{\text{rev}} + d(pV) - TdS = dw_{\text{rev}} + d(pV)$$

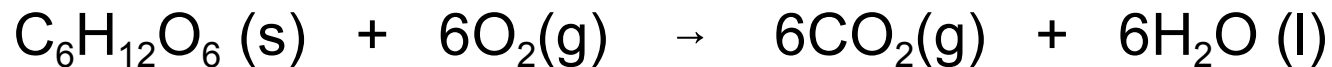
Work consists of expansion work, $w_{\text{rev}} = -p dV$, and some other kind of work (e.g., electrical work pushing electrons through a circuit, work raising a column of fluid, etc.). The latter work is **non-expansion work**, dw_e

$$\begin{aligned} dG &= (-p dV + dw_{e,\text{rev}}) + p dV + V dp \\ &= dw_{e,\text{rev}} + V dp \end{aligned}$$

And, if work occurs at constant p , then $dG = dw_{e,\text{rev}}$; 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)? $\Delta_r S^\circ = +182.4 \text{ J K}^{-1} \text{ mol}^{-1}$



The non-expansion work available from the combustion can be calculated from the **standard Gibbs energy**, $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$

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

so, $w_{e, \text{max}} = -2865 \text{ kJ mol}^{-1}$ 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 $\Delta_f G^\circ$

$$\Delta_r G^\circ = \sum_{\text{products}} \nu \Delta_f G^\circ - \sum_{\text{reactants}} \nu \Delta_f G^\circ = \sum_J \nu_J \Delta_f G^\circ(J)$$

$\Delta_f G^\circ = 0$ for elements in their reference states, since their formation is a null reaction (see Table 4.4 Atkins 6th Edition, or CRC Handbook)

Calorimetry (for ΔH directly and 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