

Thermodynamics

Some Important Topics

First Law of Thermodynamics

Internal Energy U (or E)

Enthalpy H

Second Law of Thermodynamics

Entropy S

Third law of Thermodynamics

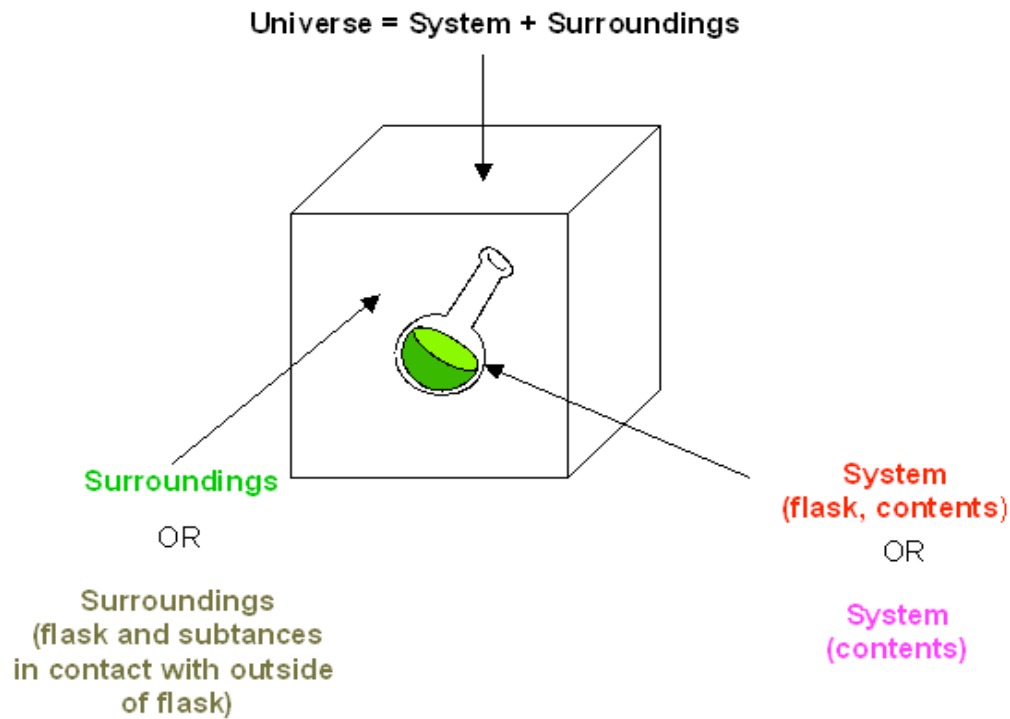
Absolute Entropy

Gibbs Free Energy G

Standard Free Energy

Calculation of ΔU , ΔH , ΔS , and ΔG

Universe, System and Surroundings



<http://employees.csbsju.edu/hjakubowski/classes/ch331/lipidstruct/systemsurr.gif>

System- that part of the universe of interest

Ex. liquid in a beaker

Questions of interest for physical and chemical changes

1. Will reaction occur? Is it spontaneous?
2. To what extent will reaction go to completion? What are the equilibrium amounts of reactants and products?
3. How fast will reaction go?

For above questions can use Thermodynamics to answer 1 and 2 (how far?) but must use kinetics to answer question 3 (how fast?)

Kinetics is study of rate of change and will be covered in another chapter

First Law of Thermodynamics

First Law is the idea of Conservation of Energy
which is

Energy can be converted from one form to another but cannot be created or destroyed.

or

Energy of the universe is constant.

or

You can't get something for nothing.

This law is very general but very important.

It helps us understand the type of change that can occur in our universe.

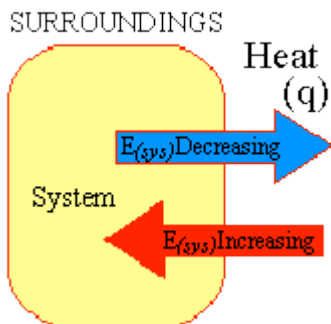
For thermodynamic studies we need to divide the universe into two parts called: the system (part we are investigating) surroundings (everything else)

The total energy of a system is the internal energy of a system (**E** or **U**) and includes all the ways that energy might be stored including the kinetic energy of molecular motion and atomic vibrations and the potential energy stored in chemical bonds.

(some books use **E** and some use **U** for internal energy symbol – we will use **E**)

Thermodynamics and change

System Change is based on going from initial state \rightarrow to final state
and ALWAYS write **change = (final – initial)**



<http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch5/work.html>

Note: same for work (w out then ΔU decrease) and (w in then ΔU increase)

Note: Properties that can be expressed as (final – initial) and we write with Δ such as $\Delta U = U_f - U_i$ are called state functions. Properties that you cannot calculate by just knowing final and initial states but must know how process occurred are called path functions.

Important State Functions are: ΔT , ΔH , ΔE , ΔS , and ΔG and

Important Path Functions are: q and w.

Second law of thermodynamics and Entropy

Water at room temperature does not freeze, why?

First Law (conservation of energy) allows if room gets hotter and water colder then energy is conserved, but it does not happen so need another law.

Second law deals with **entropy S** which is a measure of randomness

Tells us whether a process or chemical reaction can occur.

First law:

Chemical or physical change cannot occur unless energy of universe remains constant. No exceptions have ever been found.

Second law:

Chemical or physical change cannot occur unless the entropy of the universe increases. No exceptions have ever been found.

Spontaneous change is associated with entropy increase

No change can occur which causes entropy of universe to decrease

Entropy (S) is the measure of randomness and disorder.

Entropy change examples:

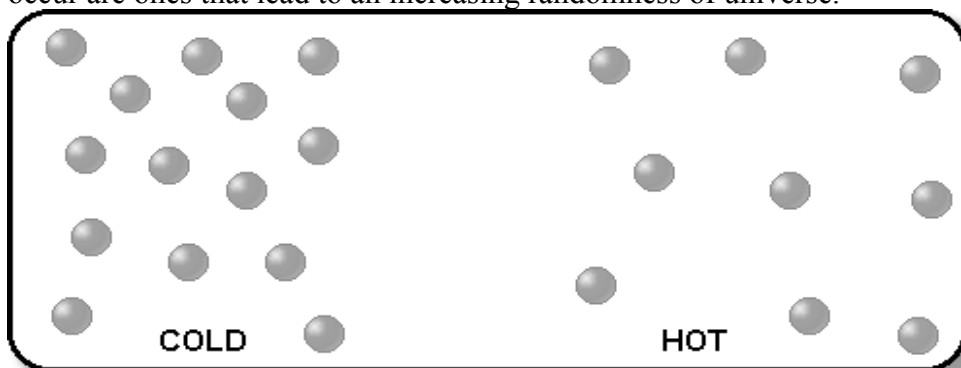
Molecules of gas at high pressure always spread to lower pressure regions.

Gas in balloon spreads out into room and deflates but never see balloon spontaneously fill with air.

Heat always goes from high temperature into cooler regions.

Hot coffee in a room gets cooler and the heat spreads out into the room, but never see a cold cup of coffee spontaneously warm up.

The spreading out of more concentrated molecules and the spreading out of more concentrate energy are changes from more order to more random. Changes that occur are ones that lead to an increasing randomness of universe.



← heat ← (direction of heat flow)

<http://www.physchem.co.za/Heat/Effects.htm>

At high enough temperature spontaneous change is

Solid → Liquid → Gas

because gas more random than liquid and liquid more random than solid

Increase entropy (S) of system by going from solid to liquid to gas

Must consider

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

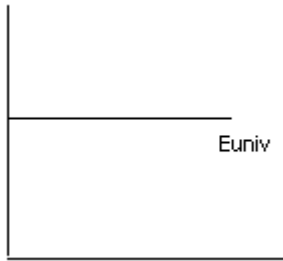
Entropy change of universe is sum of change for system and surroundings

ΔS_{sys} can decrease but only if ΔS_{sur} increases by more

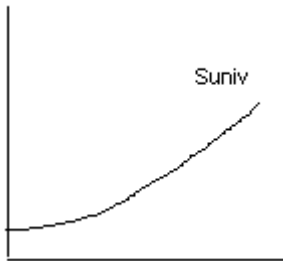
If at a stable equilibrium then $\Delta S_{\text{sys}} = 0$ and no change occurs

First, Second, and Third Law

1st Law – Energy of Universe is constant.



2nd Law – Entropy of Universe increases.



Third Law of Thermodynamics

At absolute zero (Temp = 0 K = -273.15 °C), the entropy of a perfect crystal is 0.

A solid like glass that has imperfections built into it will not have an entropy of 0 even at 0 K because not a perfect crystal so still has some randomness left in it

Another way to say third law is - **It is NOT possible to reach absolute zero**

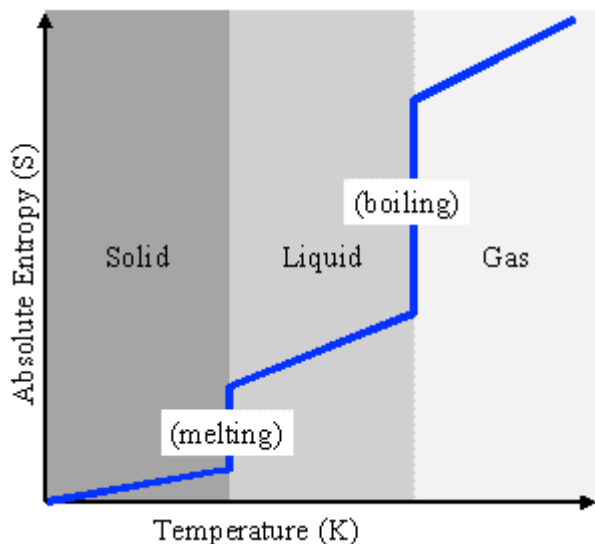
Note: At absolute zero all atomic motion stops atoms and molecules are no longer vibrating around or moving past each other. However, it is harder and harder to lower temperature as you get closer and closer to absolute zero. Even though scientists cannot quite reach (T=0 K) it is a useful reference point.

Absolute Entropies

Reference point for entropy of substance is entropy at zero Kelvin

Entropy increases as temperature increases creating more randomness.

Lowest entropy occurs at $T = 0\text{K}$ (zero Kelvin) = -273.15°C so therefore this is lowest entropy [$S = 0\text{ J/K mol}$ at $T = 0\text{ K}$]



<http://wine1.sb.fsu.edu/chm1046/notes/Thermody/MolBasis/MolBasis.htm>

Thermodynamic tables have absolute entropy of substances at 25°C and 1 atm
But reference point is $S = 0\text{ J/K}$ for 1 mol of substance at 0 K

ΔH_f° for element is 0 at standard state 25°C and 1 atm

S° for element is **not** equal to 0 at 25°C and 1 atm

ΔH_f° for compound is based on formation from elements

S° for compound is **not** based on formation from elements

Entropy will be 0 only at -273°C not at 25°C

So entropy of pure element is not zero at standard state!

Do not assume entropy zero for element – have to look up value.

Use absolute entropies to calculate ΔS entropy change for reaction

Entropy changes we are now calculating are **for system** and can be positive or negative

Entropy change calculation is

$$\Delta S^\circ = \Sigma S^\circ (\text{products}) - \Sigma S^\circ (\text{reactants})$$

and remember the greater the value of ΔS then the greater the increase in the randomness of the system.

Example:

Calculate ΔS° for reaction.



then (and notice to simplify writing we have dropped ° symbol but understand that values are at standard state)

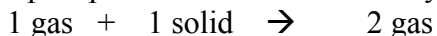
$$\Delta S = \Sigma S (\text{products}) - \Sigma S (\text{reactants})$$

$$\Delta S = [2 (206.3)] - [1 (130.6) + 1 (116.7)] \quad \text{units are } \text{mol(J/ K mol)} = \text{J/K}$$

$$\Delta S = [412.6] - [247.3]$$

$$\Delta S = +165.3 \text{ J/K}$$

We might expect positive value for ΔS for system because change



should increase randomness (entropy) because gas more random than solid.

Note: In general more randomness if gas or if temperature higher or if a much larger molecule rather than smaller.

Methods to determine change in Gibbs Free Energy (ΔG)

1. $\Delta G = \Delta H - T \Delta S$ if have data to find ΔH and ΔS
2. $\Delta G = \Sigma \Delta G_f(\text{prod}) - \Sigma \Delta G_f(\text{react})$ if have ΔG of formation data
3. ΔG using Hess's Law from ΔG for known reactions.

Gibbs Free Energy

To predict changes, focus on system

Use Gibbs free energy for chemical reaction at constant temp and pressure.

Gibbs free energy is defined as

$$G = H - TS$$

and

$$\Delta G = \Delta H - T\Delta S \quad \text{Very Important Equation}$$

unless told otherwise ΔH , ΔS and ΔG refer to system at 25°C.

Most of our calculations are for values of ΔG at 25°C (298 K)

Note: If ΔS_{univ} is (+) for universe then ΔG for system is (-) so measure of system ΔG is more convenient way to predict change.

<u>ΔS_{univ}</u>	<u>ΔG</u>	<u>ΔS_{univ}</u>	<u>Reaction</u>
+	-	increase	spontaneous, will go
0	0	stay same	no change at equilibrium
-	+	decrease	not spontaneous, not go (but reverse will)

If you want to know why from math proof (can skip)

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

and equation for calculating is $\Delta S = \Delta H/T$

and ΔH_{sys} heat change for system is $-\Delta H_{\text{sur}}$ for surroundings so

$$\Delta S_{\text{sur}} = -\Delta H_{\text{sur}}/T = -\Delta H_{\text{sys}}/T$$

so

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

becomes

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}}/T$$

and multiple both sides by $-T$

$$-T\Delta S_{\text{univ}} = -T\Delta S_{\text{sys}} + \Delta H_{\text{sys}}$$

and if we define new function Gibbs free energy as

$$\Delta G = -T\Delta S_{\text{univ}} = -T\Delta S + \Delta H$$

And results you need to know

$$\Delta G = \Delta H - T\Delta S$$

units are

$$\Delta G = \Delta H - T\Delta S$$

$$= (\text{kJ}) - (\text{K})(\text{J/K})(\text{kJ}/1000\text{J}) = \text{kJ} \text{ for reaction as written or kJ/mol in tables}$$

unless told otherwise symbols ΔH , ΔS , and ΔG refer to the system

**So if entropy of universe increases then ΔG of system will decrease!
The direction of spontaneous change is negative ΔG for system!**

ΔG tells us if change can occur for chemical reaction!

Calculate ΔG from Standard Free Energies

ΔG_f° standard free energy of formation

25°C and 1atm

for 1 mol compound formed from elements

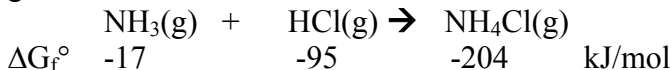
Use ΔG_f° to get ΔG just like used ΔH_f° to get ΔH for reaction.

Standard free energy of element in standard state is 0.

$$\Delta G = \Sigma \Delta G_f(\text{prod}) - \Sigma \Delta G_f(\text{react})$$

Example:

given



then find ΔG

$$\Delta G = \Sigma \Delta G_f(\text{prod}) - \Sigma \Delta G_f(\text{react})$$

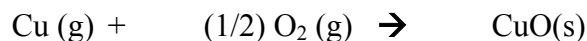
$$\Delta G = [1(-204)] - [1(-17) + 1(-95)] \text{ where units are } 1\text{mol}(-95\text{kJ/mol}) = -95\text{kJ} \text{ etc}$$

$$\Delta G = -92 \text{ kJ}$$

so since $\Delta G < 0$ the reaction will go (will occur) (products form)

Example

Will this reaction occur at 298K ?



ΔG_f° for Cu and O_2 are zero since pure elements

and in Table find $\Delta G_f^\circ = -127\text{kJ/mol}$ so

$$\Delta G = \Sigma \Delta G_f(\text{prod}) - \Sigma \Delta G_f(\text{react})$$

$$\Delta G = [1(-127)] - [1(0) + (1/2)(0)] \text{ where units are } 1\text{mol}(-127\text{kJ/mol})$$

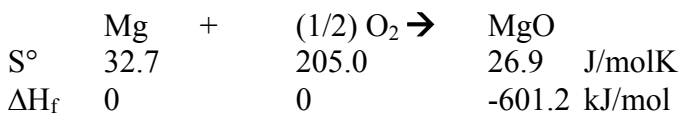
$$\Delta G = -92 \text{ kJ/mol}$$

so negative ΔG means reaction will occur but we observe that it is very slow at room temperature (can take years for penny to get CuO coating and turn brown)

Can speed up reaction by raising temperature (Kinetics chapter)

Determine ΔG

old Magicube camera flash bulb (1960s) used Mg metal sealed in bulb with oxygen so reaction is:



$$\begin{aligned} \Delta S &= [S_{\text{MgO}}] - [S_{\text{Mg}} + (1/2) S_{\text{O}_2}] \\ &= [26.9] - [32.7 + (1/2)(205.0)] \\ &= -108.3\text{J/K} \end{aligned}$$

$$\begin{aligned} \Delta H &= \{\Delta H_f \text{MgO}\} - \{\Delta H_f \text{Mg} + (1/2) \Delta H_f \text{O}_2\} \\ &= [-601.2] - [1(0) + (1/2)(0)] \\ &= -601.2\text{kJ} \end{aligned}$$

$$\begin{aligned}
\Delta G &= \Delta H - T\Delta S \\
&= -601.2\text{kJ} - (298\text{K}) (-108.3\text{J/K}) (1\text{kJ}/1000\text{J}) \\
&= -601.2 + 32.3\text{kJ} \\
&= -568.9\text{kJ}
\end{aligned}$$

and since ΔG is negative reaction will form MgO

Look up $\Delta G_f(\text{MgO}) = -569\text{kJ}$ based on

$$\Delta G = [\Delta G_f(\text{MgO})] - [\Delta G_f(\text{Mg}) + (1/2) \Delta G_f(\text{O}_2)]$$

this reaction occurs rapidly once initiated

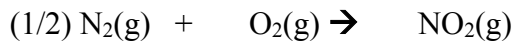
Combinations of possible signs shown below

Occur	ΔG	=	ΔH	$T\Delta S$	Occur
Yes	-		-	+	YES
No	+		+	-	NO
	?		+ no	+ yes	can (at higher T)
	?		- yes	- no	can (at lower T)

Example of Application

Should you invest in an engine that is said to burn air at room temperature?

Told that a special chamber allows O₂ to combine with N₂ to form NO₂ (nitrogen dioxide) using reaction



Evaluate using thermodynamics

Calculate enthalpy change

$$\begin{aligned} \Delta H^\circ &= \sum \Delta H_f^\circ (\text{prod}) - \sum \Delta H_f^\circ (\text{react}) \\ &= [(+34)] - [(0 + (1/2)(0))] \\ &= +34 \text{ kJ} \end{aligned} \quad \text{so no heat given off only taken in !}$$

Calculate entropy change

$$\begin{aligned} \Delta S &= [(1) S_{\text{NO}_2}] - [(1/2) S_{\text{N}_2} + (1) S_{\text{O}_2}] \\ &= [(1) 240.5] - [(1/2)(191.5) + (1) 205.0] \\ &= 240.5 - 300.8 \\ &= -60.3 \text{ J/K} \end{aligned}$$

Calculate Gibbs Free energy change from above

$$\begin{aligned} \Delta G &= \Delta H - T \Delta S \\ \Delta G &= +34 \text{ kJ} - (298 \text{ K}) (-60.3 \text{ J/molK}) (1 \text{ kJ}/1000 \text{ J}) \\ &= 34 \text{ kJ} + 18.0 \text{ kJ} \\ &= +52 \text{ kJ} \end{aligned}$$

Reaction will NOT occur and NO heat is given off.

Note that neither ΔH which is + or ΔS which is - favors reaction

Temperature Effect

ΔG can be found for different temperature values

using $\Delta G = \Delta H - T\Delta S$

remember can get

ΔS° from S° values in Table for reactants and products

ΔH° from ΔH_f° values in Table for reactants and products

ΔH , ΔS will vary with temp. but frequently variation is small so...

Calculation we do **will assume no variation in ΔH or ΔS but only in T and ΔG .**

Example:

Given $\Delta H^\circ = +177\text{kJ}$ $\Delta S^\circ = +285\text{J/K}$
for reaction $\text{NH}_4\text{Cl(s)} \rightarrow \text{NH}_3\text{(g)} + \text{HCl(g)}$

Find ΔG° (25°C) and ΔG (500°C)

For $T = 25^\circ\text{C}$ then $T = 298\text{K}$

$\Delta G = \Delta H - T\Delta S$

$\Delta G^\circ = \Delta H - T\Delta S = 177\text{kJ} - 298(285\text{J/K})(1\text{kJ}/1000\text{J})$

$\Delta G^\circ(298\text{K}) = +92\text{kJ}$ so reaction will not occur

For $T = 500^\circ\text{C}$ then $T = 773\text{K}$

$\Delta G = \Delta H - T\Delta S$

$\Delta G(773\text{K}) = 177\text{kJ} - 773(285\text{J/K})(1\text{kJ}/1000\text{J})$

$\Delta G(773\text{K}) = -43\text{kJ}$

so reaction will occur and NH_4Cl will decompose to products

What we learn is that at high enough temperature, the entropy change will dominate the enthalpy change term.

Application Example at what temp will a reaction occur?

Given data

	N ₂	O ₂	NO	
ΔH_f	0	0	90	kJ/mol
S°	192	205	211	J/K mol

can find for $N_2(g) + O_2(g) \rightarrow 2NO(g)$

$$\Delta H = + 180 \text{ kJ}$$

$$\Delta S = + 25 \text{ J/K} \quad (\text{do calculations and see if get the same numbers})$$

and that

$$\Delta G = \Delta H - T\Delta S$$

so to just reach equilibrium where $\Delta G=0$

$$0 = +180 \text{ kJ} - [(T) (+ 25 \text{ J/K}) (\text{kJ}/1000\text{J})]$$

If ΔH , ΔS do not change then solve for T

$$T = [180\text{kJ}] / [0.025\text{kJ}]$$

$$T = 7200\text{K}$$

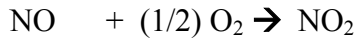
So if $T > 7200\text{K}$ then ΔS dominates and reaction will occur.

In lightning bolt very high temperatures are created and nitrogen oxide can be formed in atmosphere.

Remember ΔH , ΔS are different at high temp but we are assuming the same for calculation.

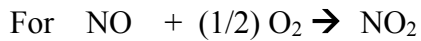
Application Example - find ΔH , ΔS , and ΔG :

Is this reaction exothermic and is it spontaneous?



Given

	NO	+	O ₂		NO ₂	
ΔH_f	90		0		+34	kJ/mol
S	211		205		240.5	J/K mol



$$\Delta S = [(1) (240.5)] - [(1) (211) + (1/2) (205)]$$

$$\Delta S = -73 \text{ J/K}$$

$$\Delta H = [(1) (34)] - [(1) 90 + (1/2) (0)]$$

$$\Delta H = -56 \text{ kJ}$$

$$\Delta G = \Delta H - T\Delta S$$

$$= -56 \text{ kJ} - (298 \text{ K}) (-73 \text{ J/K}) (1 \text{ kJ}/1000 \text{ J})$$

$$= -56 \text{ kJ} + 21.8$$

$$\Delta G = -34.2 \text{ kJ}$$

So this reaction is exothermic $\Delta H = -$

and becomes more ordered (less gas) $\Delta S = +$

and is spontaneous at 298 K $\Delta G = -$