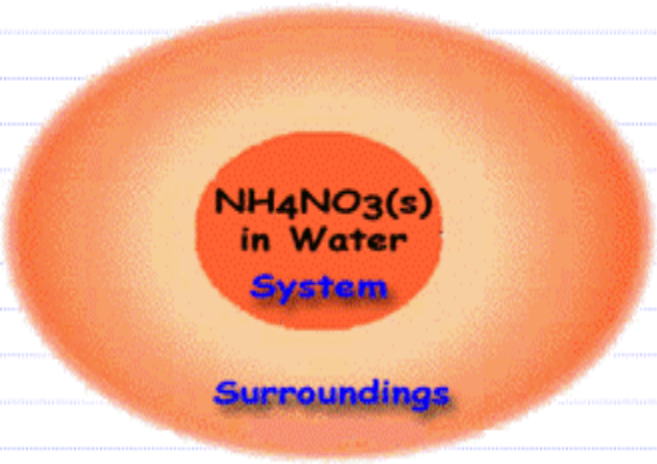
19.1 Entropy

Entropy a Measure of Spontaneity?

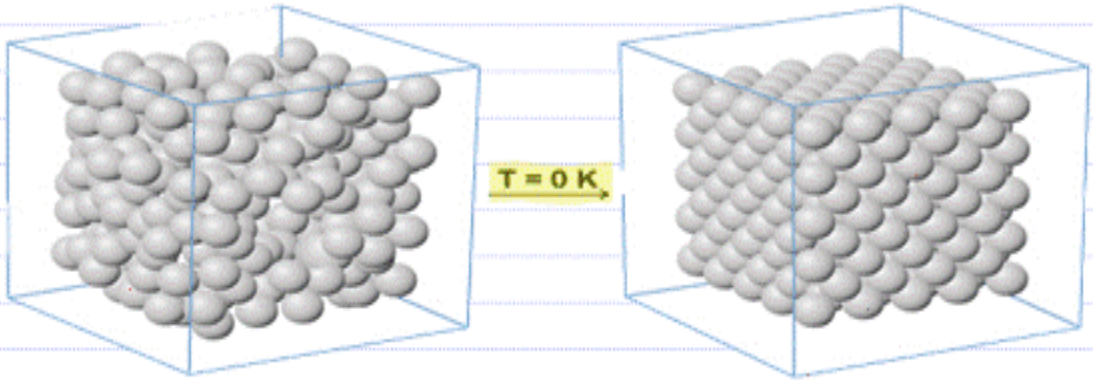


ENTROPY (S): a measure of disorder and the natural tendancy of all things to become disordered! *

SPONTANEOUS PROCESS: $\Delta S_{UNIVERSE} > 0$

$\Delta S_{UNIVERSE} = \Delta S_{SYSTEM} + \Delta S_{SURROUNDINGS} > 0$

* Even as teens we knew about Entropy though not by Name! How often were you told to tidy your Room? When we eventually did it, it took time and effort only to have it become a mess again with very little effort. Little did we know back then that it was a no win battle as we were battling ENTROPY !!



all motion stops.

3RD LAW OF THERODYNAMICS :-

The Entropy of a pure crystaline system at 0K = 0

19.1 Entropy

Trends in Entropy

- **S°(gases) >> S°(liquids) > S°(solids).**

This one is self explanatory

- **The entropy of a substance increases with temperature.**

Increase T, increase motion (vibrations) and thus increase Entropy.

- **The more complex the molecule, the greater the value of S°.**

The larger the molecule the more vibrating parts it has, the greater the Entropy.

- **Entropies of ionic solids depend on coulombic attractions.**

The smaller the force of attraction (more vibrations) the greater the Entropy : NaCl > CaO
Use the Web and look at two springs :-
a) a 'Slinky' ... small force of attraction ... ability to vibrate ?
b) 'Shock Absorber ... strong FA ... it's ability to vibrate ?

- **Entropy usually increases when a pure liquid or solid dissolves in a solvent.**

This one speaks to itself.

19.1 Entropy

Trends in Entropy

Which of the following would you expect to have the highest entropy?

a) $CO_2(g)$ ✓ **b)** Al(s)
c) $CH_3COOH(l)$ **d)** HCOOH(l)

a) Obvious since it is the only gas.

? How about ordering the remainder ?

b) Would have the smallest entropy ... only solid in the group.

? Left with CH_3COOH and HCOOH, both liquids.

c) Highest entropy of these 2 goes to the bigger one, the one with the largest Molar Mass ... CH_3COOH.

So ordering all 4 from highest entropy to lowest ...

$CO_2 > CH_3COOH > HCOOH > Al$

Which of the following would you expect to have the smallest entropy?

a) NaBr(s) **b)** MgO(s) ✓
c) NaCl(s) **d)** NaF(s)

Notice that all are solids. So lets see if any stand out with respect to magnitude of charges.

b) MgO(s), Mg^{2+} and O^{2-}

Lets now look at whats left, NaBr, NaCl and NaF, all +1/-1

Now it is size that plays the role and since the cation is Na^+ in all 3, we can look at the anion. The smaller the anion the greater the force of attraction (Coulombs Law) and the smaller the entropy.
Thus for these 3: NaF < NaCl < NaBr

So overall:

MgO < NaF < NaCl < NaBr

19.2 Calculating Entropy Change

Standard Entropy Change for a Phase Change

$$\Delta S_{\text{phase change}} = -\frac{\Delta H_{\text{PHASE CHANGE}}}{T_{\text{PHASE CHANGE}}}$$

Calculate the entropy change when 3.48 moles of ether condenses at its boiling point of 34.6 °C.

ΔH_{vap} of Ether = 26.5 kJ.mol^{-1}

a) 1 b) 2 c) 3 d) 4 e) 5

ΔS = ?00 J/K

$\Delta S = S_{final} - S_{initial}$

Condensation : g → l

$\Delta S = S_{liquid} - S_{gas}$

$\therefore$ We expect $\Delta S < 0$

$$\Delta S_{condense} = -\frac{\Delta H_{VAP}}{T(K)}$$

$$= -\frac{3.48^{*}(26{,}500)}{307.6}$$

$$= -300\ J/K$$

* Common mistake, forgetting to take into consideration the number of moles.

19.2 Calculating Entropy Change

Entropy Change in the Surroundings

UNIV = UNIVERSE
SYS = SYSTEM
SURR = SURROUNDINGS
RXN = REACTION

$\Delta S_{UNIV} = \Delta S_{SYS} + \Delta S_{SURR}$

$$\Delta S^\circ_{RXN} = \sum S^\circ_{(PRODUCTS)} - \sum S_{(REACTANTS)}$$

$\Delta S_{SURR} = -\frac{q_{SYS}}{T}$, @ constant pressure

↳ $q_{SYS} = \Delta H_{RXN}$

$\Delta S_{SURR} = -\frac{\Delta H_{RXN}}{T}$

$$\Delta S^\circ_{UNIV} = \Delta S^\circ_{RXN} - \frac{\Delta H^\circ_{RXN}}{T}$$

For a Spontaneous Process, $\Delta S_{UNIV} > 0$, and the reaction would be product favored.

Food for thought :-

ΔS_{RXN} is in J.

ΔH_{RXN} is in kJ.

and we could have a Battle between Entropy and Enthalpy.

$$\Delta S_{UNIV} = \Delta S_{RXN} - \frac{\Delta H_{RXN}}{T}$$

Let me rewrite this just a little

$$\Delta S_{UNIV} = \left(\Delta S_{RXN}\right) + \left(-\frac{\Delta H_{RXN}}{T}\right)$$

Entropy vs Enthalpy

Battle	$\Delta S > 0$	$\Delta H > 0$	Endothermic
	$\Delta S < 0$	$\Delta H < 0$	Exothermic
No Battle 1.	$\Delta S > 0$	$\Delta H < 0$	
2.	$\Delta S < 0$	$\Delta H > 0$	

1. $\Delta S_{UNIV} = + + +$; always > 0
2. $\Delta S_{UNIV} = - + -$; always < 0

19.2 Calculating Entropy Change

Entropy Change in the Surroundings

Consider the reaction $N_2(g) + 2H_2O(l) = 2NO(g) + 2H_2(g)$

for which $\Delta H^o = 752.2$ kJ and $\Delta S^o = 351.6$ J/K at 298.15 K

a) At 298.15 K is this reaction product or reactant favored?

b) Is the answer to a) entropy or enthalpy driven?

$\Delta S^\circ_{UNIV} = \Delta S^\circ_{SYS} + \Delta S^\circ_{SURR}$

$\Delta S^\circ_{SYS} = \Delta S^\circ_{RXN} = 351.6$ J/K

$$\Delta S^\circ_{SURR} = -\frac{\Delta H^\circ_{RXN}}{T}$$

$$= -\frac{752,200}{298.15}$$

$= -2,522.8$ J/K

$\Delta S^\circ_{UNIV} = 351.6 - 2,522.8$

$= -2171.2$ J/K

$\Delta S^\circ_{UNIV} < 0$, ∴ this reaction is nonspontaneous and is reactant favored.

b) To answer this we need to look at what caused $\Delta S^\circ_{UNIV} < 0$.

$\Delta S^\circ_{SYS} = \Delta S^\circ_{RXN}$ is > 0

$\Delta S^\circ_{SURR} = -\frac{\Delta H^\circ_{RXN}}{T} < 0$ and it is the magnitude of ΔH°_{RXN} that is driving this.

Thus ΔS°_{UNIV} being < 0 is enthalpy driven.

Could we make this reaction spontaneous? Yes if we could reduce the magnitude of ΔS°_{SURR} which could be accomplished by running the reaction at a much higher temperature.

A rough estimate by me indicates $T = 2,140$K needed to do it! Somewhat unrealistic in this case.