Entropy and 2nd Law of Thermodynamics

CHEM 102
T. Hughbanks

Einstein's view

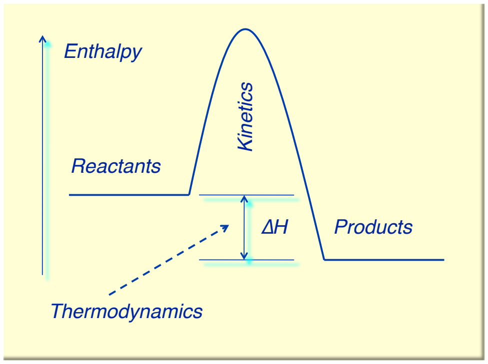
> " [Thermodynamics is] the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown."

Thermodynamics

Review of some Thermodynamic Concepts

- *First law of thermodynamics:* The law of conservation of energy; energy cannot be created or destroyed.
- State Function: Quantity in which its determination is *path independent*.
- $\Delta U = q + w$: The change in internal energy of a system is a function of heat and work done on or by the system.
- ΔH: Heat transferred at constant pressure.
- Exothermic Process: $\Delta H < 0$
- Endothermic Process: $\Delta H > 0$

Thermodynamics & Kinetics



Entropy & the Second Law of Thermodynamics

Spontaneity

- Spontaneous: "Occurring without outside intervention."
- A reaction or change of state is said to be spontaneous if it is thermodynamically allowed.
- For a chemist, prediction of spontaneity is a major goal of thermodynamics.

Factors Affecting Spontaneity

- Energy or Enthalpy: ∆U or ∆H
  - Not a good predictor. Both endothermic and exothermic reactions can occur.
- Temperature
  - Some processes are spontaneous only at certain temperatures.
- Concentrations, pressures, etc.

Entropy

- Entropy (S) is a thermodynamic state function which can be described qualitatively as a measure of the amount of disorder present in a system.
- From a chemical perspective, we usually mean *molecular* disorder.
- Increases in the entropy of a system are usually (not always) accompanied by the flow of heat into the system.

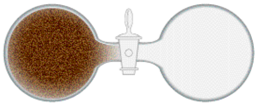
Entropy and Disorder

- Entropy is a measure of disorder.
  more disorder → greater entropy
- Entropy of a substance depends on physical state. $S_{gas} >> S_{liquid} > S_{solid}$
- Entropy depends on temperature. Increasing T will increase entropy due to increase in molecular motion.

Entropy & Spontaneity

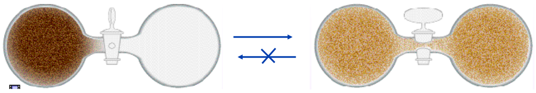
In many spontaneous processes, entropy of a system increases. ($\Delta S > 0$)

- Examples:
  - expansion of a gas into vacuum



  - mixing of gases or generation of a gas from solid or liquid reactants

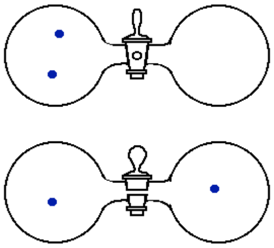
Expansion of a Gas



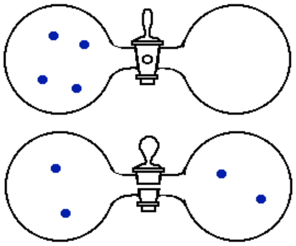
- This process obviously has a preferred direction, but why?
- Once the valve is open, the probability that all molecules will return to one side is astronomically small.
- $\Delta S > 0$ for this spontaneous change

Probabilities and Entropy

Probability that both molecules will be on left hand side: $(^1/_2)^2 = {}^1/_4$.

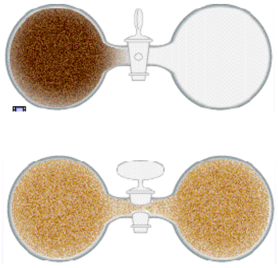


Probabilities and Entropy



Probability that both molecules will be on left hand side: $(^1/_2)^4 = {}^1/_{16}$.

Probabilities and Entropy



Probability that both molecules will be on left hand side: $(^1/_2)^N$

= A very small number when N is Avogadro's number!

Dispersal of Energy: Entropy

Boltzmann: As the number of microstates increases, so does the entropy of the system.

$$S = k \cdot \ln W$$

k = Boltzmann's constant (1.381 × 10^{-23} J/K)
W = the number of microstates corresponding to the observed macroscopic state of a system

Extra Details

Number of ways of having $N/2$ molecules on each side:

$$W_{N/2} = \begin{pmatrix} N \\ N/2 \end{pmatrix} = \frac{N!}{[(N/2)!]^2}$$

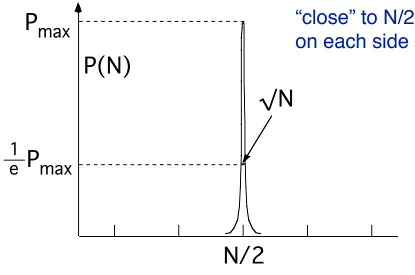
Number of ways of having $N/2 - \sqrt{N}$ molecules on one side:

$$\begin{pmatrix} N \\ N/2 - \sqrt{N/2} \end{pmatrix} = \frac{N!}{(N/2 - \sqrt{N/2})!(N/2 + \sqrt{N/2})!}$$

$$\begin{pmatrix} N \\ N/2 - \sqrt{N/2} \end{pmatrix} \Big/ \begin{pmatrix} N \\ N/2 \end{pmatrix} \rightarrow \frac{1}{e}, \text{ as N} \rightarrow \infty\text{; 0.369 for N = 200)}$$

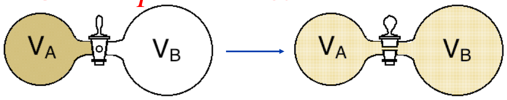
use Stirling's Approximation: $N! \approx \sqrt{2\pi N}\left(\frac{N}{e}\right)^N$ and definition of $e = \lim_{x\rightarrow\infty}\left(1+\frac{1}{x}\right)^x$

Distribution of Probabilities



Total number of outcomes "close" to N/2 molecules on each side ≈ 2^N ≈ W(N)

Gas Expansion & Probabilities



Entropy change on expansion:

$$\Delta S = k \ln W_f - k \ln W_i = k \ln (^{W_f}/_{W_i})$$

$$\Delta S = k \ln (^{V_f}/_{V_i})^N = R \ln (^{V_f}/_{V_i}) \quad (Nk = R)$$

When $V_A = V_B$, $V_f = 2V_i$, and $\Delta S = R \ln 2$

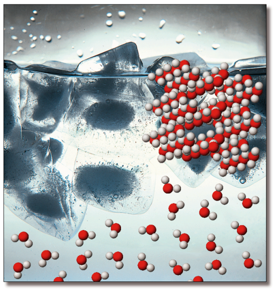
Entropy, Probabilties, Disorder

- For systems with equal energy content, those that are most disordered also turn out to be most statistically likely (most probable).
- **Entropy increases as the statistical likelihood increases.**
- The entropy of the universe tends to increase: $(\Delta S)_{universe} > 0$ in all changes

Popular Misconceptions

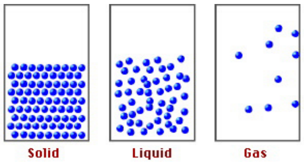
- Sometimes you see it said that "in principle, the universe could show a decrease in entropy, it is just highly unlikely" – True, but means astronomically unlikely EVER!
- The entropy of system *can* decrease, if the entropy of the universe increases. (For example, the "order" we see in life on earth is the direct result of a massive increase in the entropy of the sun.)

Dispersal of Energy: Entropy



- The entropy of liquid water is greater than the entropy of solid water (ice) at 0˚ C.
- Energy is more dispersed in liquid water than in solid water due to the lack of an ordered network as in the solid state.

Entropy & States of Matter



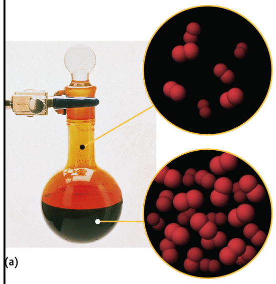
S^o (J/K•mol)	
H_2O(liq)	69.95
H_2O(gas)	188.8

S (solids) < S (liquids) < S (gases)

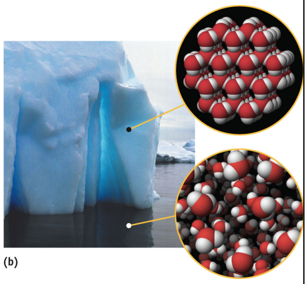
$\longrightarrow$

Energy dispersal

Entropy & States of Matter



$S^\circ(Br_2$ liq$) < S^\circ(Br_2$ gas$)$



$S^\circ(H_2O$ sol$) < S^\circ(H_2O$ liq$)$

Generation of a Gas (Demo)

- "Frozen Beaker" demo ($\Delta H > 0$):

$$Ba(OH)_2{\bullet}8H_2O(s) + 2NH_4SCN(s) \rightarrow Ba(SCN)_2{\bullet}2H_2O(s) + 2NH_3(g) + 8H_2O(\ell)$$

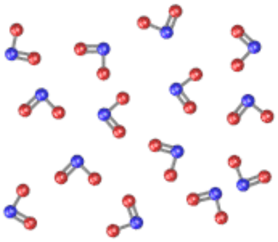
- Solid reactants → solid, liquid, & gas in products
- $\Delta S_{system} >> 0$

Entropy & Spontaneity

- In some spontaneous processes, the entropy of a system decreases. ($\Delta S < 0$)
- Examples:
  - freezing of a liquid
  - condensation of a gas
  - formation of a solid product from gas or liquid reactants
- These are common events, and they clearly have $\Delta S < 0$.

Example: $2\ NO_2 \rightarrow N_2O_4$, $\Delta S < 0$

- The conversion of 2 moles of gas into one mole of gas decreases the entropy of the system.



Second Law of Thermodynamics

- Entropy change of the *system* does not correctly predict spontaneity.
- One correct statement of the second law of thermodynamics is: **"The entropy *of the universe* is always increasing."**
- In equation form, this is: $\Delta S_{universe} > 0$.

where $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

Entropy and Heat

- Simplest case is a process which occurs at constant T. Phase changes are good examples.
- For the case of constant T (isothermal):

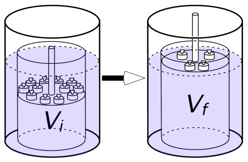
$$\Delta S = q_T/T$$

- q_T is heat at constant T, signs as usual
- From this equation, ΔS has units of J/K

How do we reconcile the "heat transfer" and statistical definitions of entropy?

Consider a Reversible Isothermal Gas Expansion:

Reversible Isothermal Expansion

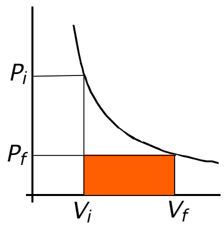


Gradually decrease pressure, by removing one weight at a time.

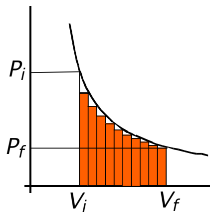
Note, since T = const., $P_i V_i = P_f V_f$

- If we gradually decrease the pressure while keeping the apparatus in a large bath, expansion will be nearly reversible and nearly isothermal.

Irreversible vs. (nearly) Reversible

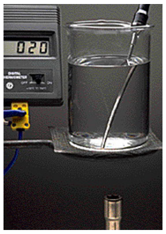


Pressure lowered in one step (remove all weights)



Pressure lowered in incremental steps

Entropy Changes for Phase Changes



For a phase change,

$$\Delta S = \frac{q_{rev}}{T}$$

where q = heat transferred in the phase change

For $H_2O\text{ (liq)} \rightleftharpoons H_2O\text{(g)}$

$$\Delta H = q = +40{,}700 \frac{J}{mol}$$

$$\Delta S = \frac{q_{rev}}{T_{boil}} = \frac{40{,}700\ J/mol}{373.15\ K} = +109 \frac{J}{mol \cdot K}$$

Illustrative Problem

- Dry ice is solid CO_2. At T = 195 K, dry ice sublimes (is converted directly from a solid into a gas). $\Delta H_{sublim.}$ = 25.2 kJ/mol
- Suppose 27.5 g of dry ice are allowed to sublime in a room with T_{room} = 26.5°C.
- Without doing calculations, predict the signs of ΔS_{CO_2}, ΔS_{room}, and $\Delta S_{universe.}$
- Calculate ΔS_{CO_2}, ΔS_{room}, and $\Delta S_{universe.}$

Spontaneity

- Second law says that a process is spontaneous if $\Delta S_{universe} > 0$.
- From problem, realize that the phase change will be spontaneous as long as the temperature of the room is above the sublimation temperature.
- At T_{sublim}, $\Delta S_{universe} = 0$, so both phases can exist in any ratio. → EQUILIBRIUM

Absolute Entropy

- We said earlier that the entropy of any material will increase as T increases, due to increased molecular motion.
- Molecular motion, and entropy, decrease as T is lowered.
- T = 0 K is the (theoretical) limit to how far we can lower the temperature.
- Thus *minimum* entropy is at 0 K.

The Third Law

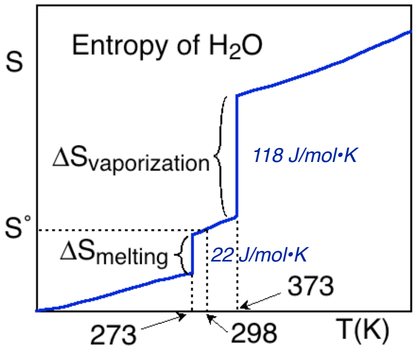
- The third law of thermodynamics says: **"The entropy of a pure, perfect crystal at 0 K is zero."**
- Applies to a crystal of any substance.
- Note that this is a fairly hypothetical limit: "pure," "perfect," and 0 K are all ideals.
- Third law means that we can find absolute entropy. (unlike E, H)

$S°$ and $\Delta S°$

- Thermo. Tables (Appendix E) give $S°$ for many substances.
  (Units of J $mol^{-1}K^{-1}$)
- This is *absolute entropy* at 25°C, 1 atm.
- Notice that $S°$ is *never* equal to zero, but approaches zero as the temperature approaches zero. $S°$ is *never* less than zero (but ΔS_{system} can be less than zero).

Entropy as a Function of Temp.

An increasing function



$S°$ and $\Delta S°$

- Easy to find $\Delta S°$ from the tabulated $S°$'s:
  $\Delta S° = S°_{products} - S°_{reactants.}$
- Useful form is:
  $\Delta S°_{rxn} = \sum nS°_{products} - \sum nS°_{reactants}$
- Similar in appearance to Hess's law.
- <u>But</u> this uses absolute $S°$ values, where for $\Delta H°_{rxn}$ we used $\Delta H_f°$'s.

Problem

- The "Mond Process" is used commercially to produce pure nickel.
  $Ni(s) + 4\ CO(g) \rightarrow Ni(CO)_4(g)$
- First, try to <u>predict</u> the signs of $\Delta S°$ and $\Delta H°$.
- Then use data on next slide to calculate values.

Data for Problem

$Ni(s) + 4\ CO(g) \rightarrow Ni(CO)_4(g)$

$\Delta S°$, $\Delta H°$ = ??

	Ni(s)	CO(g)	$Ni(CO)_4(g)$
$\Delta H_f°$	0	−110.52	−602.9
$S_{298}°$	29.87	197.56	410.6

$\Delta H_f°$ in kJ mol^{-1}, $S_{298}°$ in J K^{-1} mol^{-1}.

Watch units!