Thermo Notes #3

Entropy and 2nd Law of Thermodynamics

Monday, January 30

CHEM 102H

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Reading

- You should reading Chapter 7.
- Some of this material is quite challenging, be sure to read this material carefully.

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

- "Spontaneity" is a somewhat misleading term referring to whether a chance can occur (even in principle).
- Energy: ΔU or ΔH
  - Not good predictors. 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.

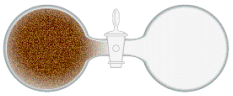
Entropy and Disorder

- 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

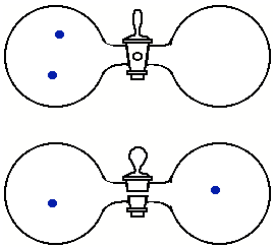


  - mixing of gases or generation of a gas from solid or liquid reactants

Expansion of a Gas

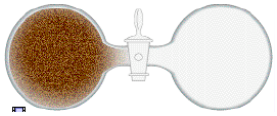
- This process obviously has a preferred direction.
- Once the valve is open, the probability that all molecules will return to one side is astronomically small.
- $\Delta S > 0$ for this spontaneous change

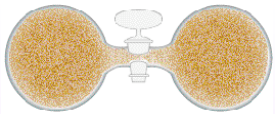
Probabilities and Entropy



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: $(1/2)^N$

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

Extra Details

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

$$\binom{N}{N/2} = \frac{N!}{[(N/2)!]^2}$$

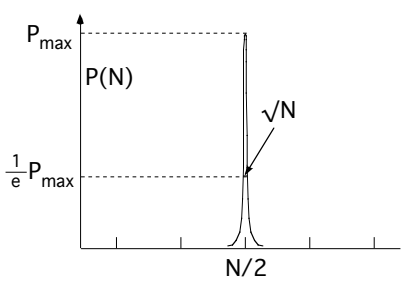
Number of ways of having $N/2 - \sqrt{N}$ molecules on one side:

$$\binom{N}{N/2 - \sqrt{N/2}} = \frac{N!}{(N/2 - \sqrt{N/2})!(N/2 + \sqrt{N/2})!}$$

$$\binom{N}{N/2} \Big/ \binom{N}{N/2 - \sqrt{N/2}} \rightarrow e, \text{ as } N \rightarrow \infty; \text{ 2.709 for N = 200)}$$

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

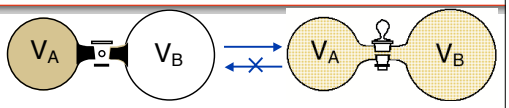
Distribution of Probabilities



Gas Expansion & Probabilities

- Once the valve is open, the probability that we'll find N molecules on one side is $(1/2)^N$. If we had started with 2N molecules, the probability would have been $(1/2)^{2N}$.

Gas Expansion & Probabilities

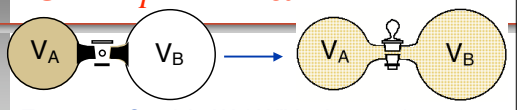


- Once the valve is open, the probability that N molecules will be found on the left side is $(V_A/(V_A+ V_B))^N = (V_i/V_f)^N$
  For 2N molecules, the probability would be $(V_i/V_f)^{2N}$.

Some notes on Nature and Probability

- For a system with a given amount of energy, the system will usually be found in its most probable state(s).
- The probabilities we've computed in gas expansion example do not scale with the size of the system, but their logarithms do scale with the size of the system.

Gas Expansion & Probabilities



- Entropy: $S = k \ln W$ ("W" is the number of system microstates of the same energy)
- $\Delta S = k \{\ln(W_{final} / W_{initial}\}$
- $W_{final} / W_{initial} = (V_f/V_i)^N$
- $\Delta S = Nk \ln (V_f/V_i) > 0 \quad (Nk = R)$ (!)

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 "disorder" of the universe tends to increase: $(\Delta S)_{universe} > 0$ in all changes

Example: Boiling and Entropy

- For $H_2O(l)$, $S^\circ = 69.91$ J• K^{-1}• mol^{-1}
- For $H_2O(g)$, $S^\circ = 188.3$ J• K^{-1}• mol^{-1}
- Therefore $\Delta S^\circ_{vap} = 118.4$ J• K^{-1}• mol^{-1} (at 298 K)
- Problem: At 373 K, $\Delta S_{vap} = 109$ J• K^{-1}• mol^{-1} (why different?). What part of this is due to the greater volume occupied by the vapor phase?

Generation of a Gas

- "Frozen Beaker" reaction :

$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2 \cdot 2H_2O(s) + 2NH_3(g) + 8H_2O(l)$

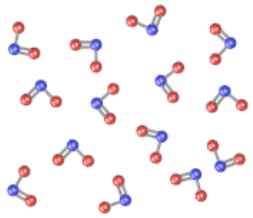
- Solid reactants → solid, liquid, & gas in products
- $\Delta S_{system} >> 0$

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: $\Delta S_{universe} > 0$.
  $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

Entropy and Heat

- Simplest case is a process which occurs at constant T. Phase changes are good examples.
- For the case of constant T,
  $$\Delta S = q_{rev}/T$$
- q_{rev} is heat transferred in a reversible process, at constant T (signs as usual)
- From this equation, ΔS has units of J/K

Some Subtleties

- We've said that, for constant T,
  $$\Delta S = q_{rev}/T$$
- This is a way of calculating ΔS (ΔS_{sys} recall) even if we don't actually transfer the heat reversibly as long as in the irreversible process the state of the system is the same as it would have been in the reversible process. (!)

ΔS for Phase Changes

- Since, for constant T,

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

  and, $q_{rev} = \Delta H^\circ$ (at constant P), we can get ΔS for a phase change at the normal melting or boiling points.

Ex: For ethanol, compute ΔS_{fus} & ΔS_{vap}

$\Delta H_{fus}^\circ = 4.6$ kJ/mol; $T_m = 158.7$ K

$\Delta H_{vap}^\circ = 43.5$ kJ/mol; $T_b = 351.5$ K

Isothermal Ideal Gas Expansion

- Suppose we carry out the expansion of an ideal gas at constant temperature. Since the energy of an ideal gas depends only on temperature ΔU = 0

$$\Delta U = q + w \quad \Rightarrow \quad q = -w$$

for each infinitesimal step of the expansion, $dw = -PdV$

$$q = -\int_{V_i}^{V_f} dw = \int_{V_i}^{V_f} PdV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

$$q = nRT \ln \frac{V_f}{V_i} \quad \Rightarrow \quad \Delta S = \frac{q}{T} = nR \ln \frac{V_f}{V_i}$$

Examples

- Suppose we carry out a reversible, isothermal expansion of 1.0 mole of an ideal gas such that we double its volume. What is ΔS?
- Suppose we carry out a free expansion of 1.0 mole of an ideal gas, such that the volume the gas occupies after the expansion has doubled. What is ΔS?

Illustrative Phase Change Example

- 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 $\Delta S_{universe}$.

Entropy: Heat & Probabilities

- Why does heat transfer have anything to do with the statistical interpretation of entropy?
- The last example illustrates how the thermal definition of entropy guarantees that heat flows from hot regions to cold regions:
  $\Delta S_{sys} = q/T_{sys}$ $\Delta S_{surr} = -q/T_{surr}$
- The statistical interpretation of entropy implies that energy will tend to "spread out" over time – essentially equivalent to the thermal definition.

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.

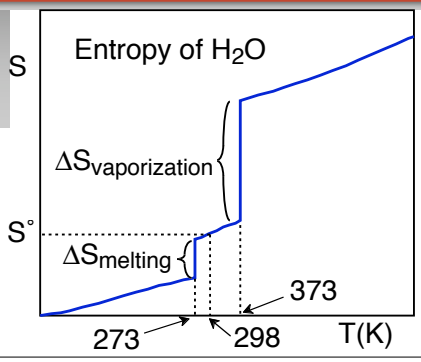
The Third Law

- 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 U, H)

S° and ΔS°

- Thermo. Tables (Appendix 2) 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 S 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 ΔS°

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

Entropy & "Degrees of Freedom"

- It is possible to make qualitative predictions concerning relative entropies by looking for 'easy degrees of freedom'. Examples:
- (prob. 7.27) Which has higher S°,
  (a) iodine or bromine? (vs. chlorine?)
  (b) cyclopentane or 1-pentene?
  (c) ethylene or polyethylene?