CHEMISTRY 24a
Winter Quarter 1997
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Lecture 5

Date: January 20, 1997

Second Law Of Thermodynamics (continued)

Different Statements of 2nd. Law

(1) $dS \geq \frac{dQ}{T}$

$$\begin{cases} \text{For reversible process: } dS = \frac{dQ_{rev}}{T} \\ \text{For irreversible process: } dS > \frac{dQ_{irrev}}{T} \end{cases}$$

Where dQ_{rev}, dQ_{irrev} denote heat delivered to system in a reversible and irreversible process respectively.

(2) W. Thomson (Lord Kelvin): It is impossible, by a cyclic process to take heat from an energy reservoir and convert it to work without at the same time transferring heat from a hot to a cold body.

or: Work cannot be extracted by a cyclic process from an energy reservoir at one temperature.

(3) Clausius' version: It is impossible by a cyclic process to transfer heat from a cold body to a hot body without also performing work

or: Heat does not flow spontaneously from a cold to a hot body.

- **Statement 2 can be understood using the cyclic process discussed earlier (Carnot cycle).**

- If T > T′, cyclic process is a heat engine, i.e., heat is extracted from reservoir at the higher temperature T, unloaded to a reservoir at the lower temperature T′, and net work obtained from system is

$$(+)nR(T-T')ln\frac{V_2}{V_1}=-W$$

Show

Step	Work = W	Heat = Q
1	$-nRTln\frac{V_2}{V_1}$ — i.e., if $V_2>V_1$, then work is done ≃ surroundings.	$Q_{input}=+nRT\ ln\frac{V_2}{V_1}$
2	$+C_V(T'-T)$	0
3	$-nRT'ln\frac{V_4}{V_3}=nRT'ln\frac{V_2}{V_1}$	$-nRT'ln\frac{V_2}{V_1}$ $\nearrow$ $Q_{unloaded}$
4	$+C_v(T-T')$	

$$W=-nR(T-T')\,ln\left(\frac{V_2}{V_1}\right)$$

$$Efficiency\ of\ Engine=\frac{Work\ Extracted}{Heat\ Input}=\frac{nR(T-T')ln\frac{V_2}{V_1}}{nRTln\frac{V_2}{V_1}}$$

$$=\frac{T-T'}{T}=1-\frac{T'}{T}=1-\frac{T_{lower}}{T_{upper}}$$

i.e., if $T_l=T_u$, work = 0

This is the maximum efficiency, because each step of the cycle is reversible.

Fraction of heat adsorbed that is unavailable to do work

$$=\frac{Q_{step\ 3}}{Q_{step\ 1}}=\frac{T_{lower}}{T_{upper}}$$

- If $T' > T$, cyclic process is a heat pump or refrigerator. There is net work done on system $= nR(T' - T)\ln\frac{V_2}{V_1}$ and heat $\left(= nRT\ln\frac{V_2}{V_1}\right)$ is pumped from the lower temperature T, and portion of this work and heat input $\left(= nRT'\ln\frac{V_2}{V_1}\right)$ is released to the reservoir at the higher temperature T'.

$$\frac{\textit{Heat pumped by system at lower temperature}}{\textit{Work done on (absorbed by) system}} = \frac{nRT\ln\frac{V_2}{V_1}}{nR(T' - T)\ln\frac{V_2}{V_1}}$$

$$= \frac{T}{T' - T} = \frac{T_{lower}}{T_{upper} - T_{lower}}$$

Statement 3 follows from this analysis.

Entropy and Disorder

We shall show later that

$$S = k_B \ln\Omega \qquad k_B = 1.380 \times 10^{-23}\, JK^{-1} \quad (\underline{\text{Boltzmann}}\ \underline{\text{constant}})$$

where Ω = # of system wavefunctions that could be written for the N molecules of the system at a particular E and V, or a particular T and V.

It turns out Ω is related to the number of possible distinct arrangements arising from distributing the molecules among the one-particle quantum states, <u>for a system of non-interacting molecules</u>.

More specifically,

$$S = -Nk_B \sum_{j} P_j \ln P_j + \textit{constant}$$

all one-particle quantum states

or

$$-Nk_B \sum_{j} X_j \ln X_j + \textit{constant}$$

where P_j is the probability of finding a molecule in one-particle quantum state j.

X_j is the fraction of molecules occupying one-particle quantum state j.

- **Example**

As an example, consider N non-interacting point masses, with no nuclear spin and no internal degrees of freedom (electronic, vibrational, rotational, etc.). That is, the point masses have translational energies only.

Such an idealized system is called perfect gas.

Note that an ideal gas shares some of these features, except that internal degrees of freedom are not excluded.

One-particle energy states and wavefunctions

Assume a cubic box of side L

$$\varepsilon_{nlm} = \frac{\hbar^2\left(n^2+m^2+l^2\right)\pi^2}{8mL^2} \qquad n,\ m,\ l \text{ are positive integers}$$

$\nearrow$ one-particle energies

$$\phi_{nlm}(x,y,z) = \left(\sqrt{\frac{2}{L}}\right)^3 \sin\frac{n\pi x}{L}\,\sin\frac{m\pi y}{L}\,\sin\frac{l\pi y}{L}$$

System wavefunction for N non-interacting particles Ψ_{system} for N non-interacting particles can be written as products of one-particle eigenfunctions and/or linear combinations thereof.

e.g. if all molecules are "occupying" the lowest one-particle quantum state,

i.e., $n=1$, $m=1$, $l=1$ for all molecules, then

$$\Psi_{system}(x_1, y_1, z_1;\ x_2, y_2, z_2; \ldots)$$

$$= \prod_i \phi_{111}(x_i, y_i, z_i)$$

↖ equal to coordinates of particle 1, 2, 3 ...

It is possible to write only 1 such system wavefunction

$$\therefore \Omega = 1$$

and $$S_{system} = k_B \ln \Omega = 0$$

If circumstances allow some of the particles to be distributed to higher-energy one-particle quantum states, then more Ψ_{system}'s may be written corresponding to the distinct arrangements arising from allocating the particles in the one-particle quantum states.

For example, if the *nml=211*; *nml=121*; and *nml=112* one-particle quantum states are accessible, possible Ψ_{system}'s are:

$$\left\{ \begin{array}{l} \phi_{211}(x_1, y_1, z_1) \prod\limits_{i \neq 1}^{N} \phi_{111}(x_i, y_i, z_i) \\[2ex] \phi_{121}(x_1, y_1, z_1) \prod\limits_{i \neq 1}^{N} \phi_{111}(x_i, y_i, z_i) \\[2ex] \phi_{112}(x_1, y_1, z_1) \prod\limits_{i \neq 1}^{N} \phi_{111}(x_i, y_i, z_i) \end{array} \right.$$

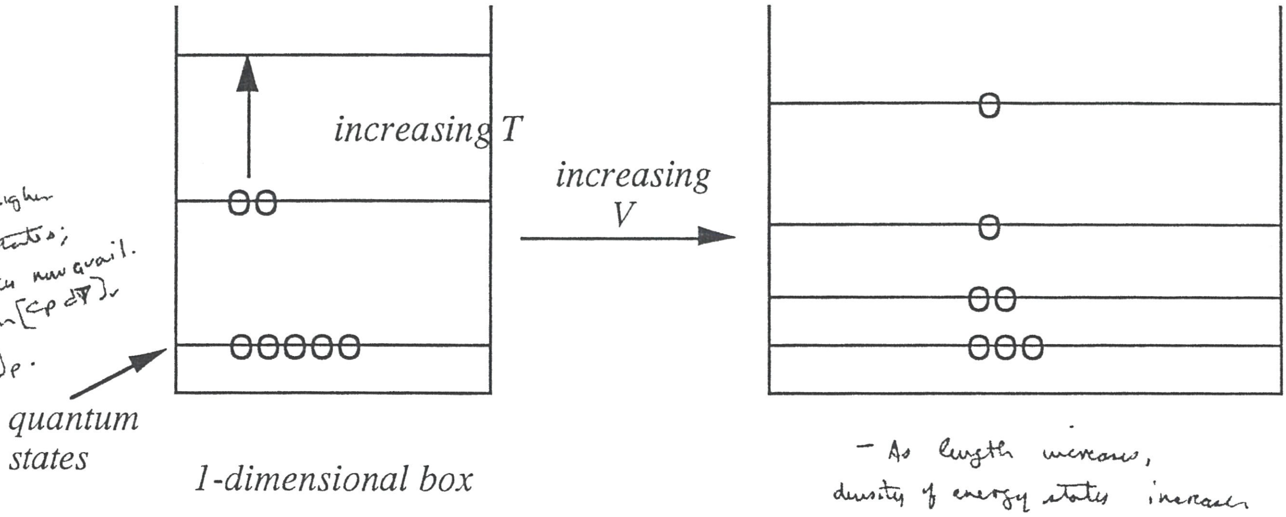
in this case, just 1 particle is not in the ϕ_{111}; there are still N particles that have ϕ_{111}.

All 3 of these states of the system have the same energy. Therefore, system degeneracy has increased.

Entropy is increased for the system.

There is more disorder.
randomness.
chaos.

• Effect of Temperature and Volume on Entropy - Molecular Interpretation.

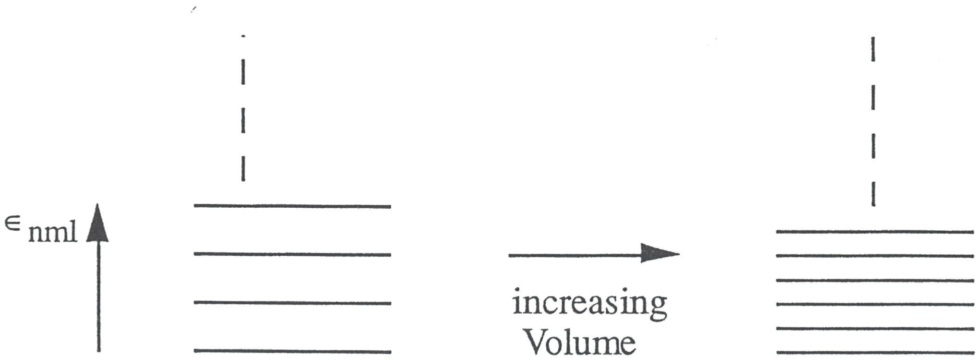


more higher energy states; # of states now avail. depends on $[C_p\, dT]_v$ or $[C_v\, dT]_p$.

– As length increases, density of energy states increases

(A) Temperature: Increasing temperature will allow the higher energy quantum states to become more accessible to the molecules. System degeneracy goes up. That is, one can write more distinct Ψ_{system} for the system; $\therefore$ S increases.

(B) Volume: Increasing volume will lower energy of the translational energy states, making more quantum states accessible to molecules at a given temperature. The one-particle energy levels become more closely packed.



Therefore, more of the one-particle energy states become accessible for a given T or E, and S increases with increasing volume. In fact,

$$\Omega = aV^N$$

so that $$\Delta S(V_1 \rightarrow V_2) = k_B ln\frac{\Omega_2}{\Omega_1}$$

$$= k_B ln\left(\frac{V_2}{V_1}\right)^N = Nk_B ln\frac{V_2}{V_1}$$

$$= nRln\left(\frac{V_2}{V_1}\right)$$

result obtained before.

Will later show that:

Absolute entropy of system

$$= -Nk\sum_{\substack{j\\ \text{all}\\ \text{molecular}\\ \text{quantum}\\ \text{states}}} X_j ln X_j \qquad + \textit{ constant}$$

for different kind of particles you have many terms.

where $x_j = \frac{n_j}{N}$

$n_j =$ *# of molecules occupying quantum state "j"*
and $Nk = n(N_A k) = nR$

So this picture of entropy unifies everything!

- **Distinguishability of Molecules**

If molecules of different chemical structure, isotopic composition, or "different color" share the same configuration space or volume, each of the distinguishable molecules will have its own set of molecular quantum states and the absolute entropy of the system will increase.

• The "Color Blind" Problem

Being "color blind" will underestimate the absolute entropy of a system.

But "color blindness" will not affect $\Delta S_{process}$ because one would be equally "color blind" in computing entropy of initial and final states!

Entropy that is "missed" or not accountable due to "color blindness" is often termed residual or latent entropy.