Biophysical Chemistry for Life Scientists

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Lecture 4
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Entropy and Free Energy. Second and Third Laws of Thermodynamics.

- **What is Entropy?**

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Entropy is a state function, or property of a system, that provides a measure of its disorder or randomness.

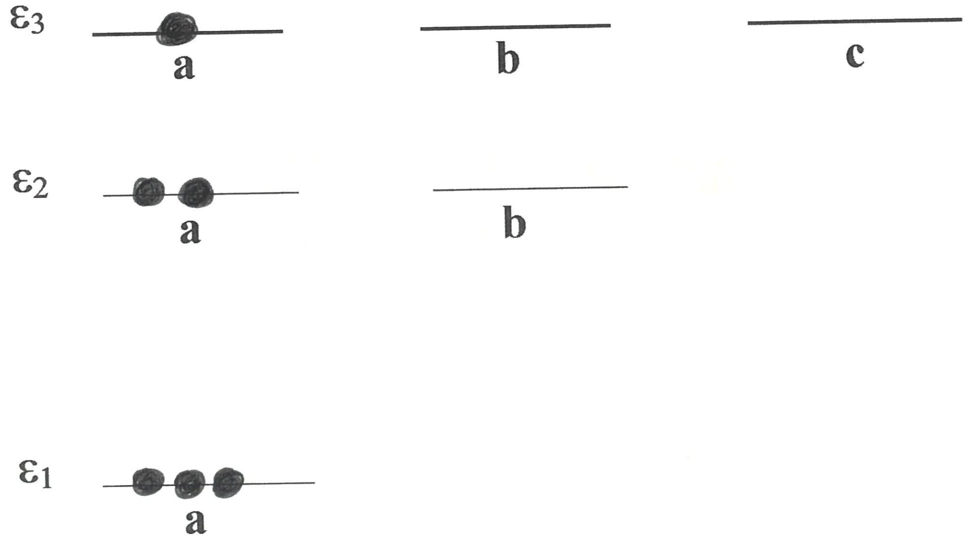
It is an extensive property. It is a function of T and V (or P), and chemical composition.

- **What do we mean by disorder or randomness?**

Illustrate by way of an example.

Return to the system of non-interacting or weakly interacting particles discussed earlier.

For simplicity, we pick a system of six non-interacting particles. Suppose, the particles occupy energy states with energies equal to ε_1, ε_2, and ε_3 as follows:



Then, $E_{system} = 3\,\varepsilon_{1a} + 2\,\varepsilon_{2a} + \varepsilon_{3a}$

$$= 3\,\varepsilon_1 + 2\,\varepsilon_2 + \varepsilon_3$$

$$N_{system} = n_{1a} + n_{2a} + n_{3a}$$

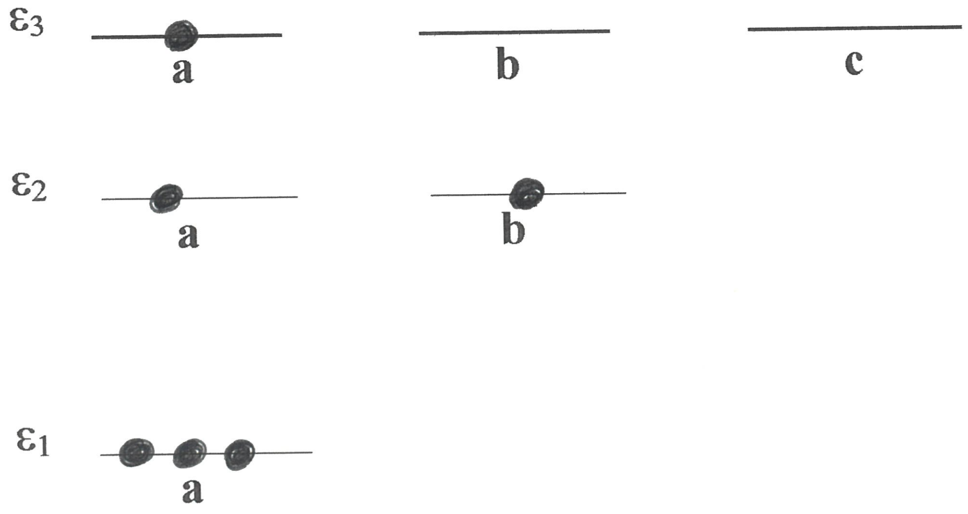
$$= 3 + 2 + 1 = 6$$

and the wavefunction for the system is

$$\Psi_1(1,2,3,4,5,6)$$

$$= \phi_{1a}(1)\,\phi_{1a}(2)\,\phi_{1a}(3)\,\phi_{2a}(4)\,\phi_{2a}(5)\,\phi_{3a}(6)$$

However, if there are degeneracies associated with the molecular energy levels, namely, there are energy states of equal energy associated with the energy levels, which is typically the case, then there are other particle distributions with the same E_{system}. For example,



Here, for this particle distribution,

$$E_{system} = 3\,\varepsilon_{1a} + \varepsilon_{2a} + \varepsilon_{2b} + \varepsilon_{3a}$$

$$= 3\,\varepsilon_1 + 2\,\varepsilon_2 + \varepsilon_3$$

$$N_{system} = n_{1a} + n_{2a} + n_{2b} + n_{3a}$$

$$= 3 + 1 + 1 + 1 = 6$$

as before, but the wavefunction for the system is different:

$$\Psi_2(1,2,3,4,5,6)$$

$$= \phi_{1a}(1)\,\phi_{1a}(2)\,\phi_{1a}(3)\,\phi_{2a}(4)\,\phi_{2b}(5)\,\phi_{3a}(6)$$

Because of equal a priori probability for the particles to occupy molecular energy states of the same energy, this particle distribution is just as likely as the first one. In other words, it is equally likely for the system to be represented by Ψ_1 or Ψ_2.

Other particle distributions are obtained by redistributing the particles among the degenerate molecular energy states associated with the energy levels, and there would be a distinct wavefunction for each.

We could generalize this to a system of N particles (N approaching N_A) with electronic, vibrational, rotational, translational degrees of freedom, where the molecular energy levels are highly packed and degenerate, as we discussed earlier. Thus, for a given E_{system}, the system could be represented by many, many system wavefunctions (Ψ_{system}), corresponding to the different ways of distributing the particles among the molecular quantum states.

To illustrate this outcome, I appeal to a system of N non-interacting particles. However, this result is completely general, and applies to any system involving large numbers of molecules. Thus, for macroscopic systems, in practice, the system has a high density of system states, namely, there are many, many Ψ_{system} 's with the same E_{system}.

- **<u>Definition of Statistical Entropy</u>**

$$\text{Statistical Entropy} \quad = \quad S \quad = \quad k_B \ln \Omega_{system}$$

where Ω_{system} is the total number of independent system wavefunctions associated with the system of N molecules for a given E_{system} and V, or a particular T and V. $k_B = 1.380 \times 10^{-23}$ J K^{-1} (Boltzmann constant) .

It turns out Ω_{system} 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,

$$S = -Nk_B \sum_{\substack{j \\ \text{all one - particle} \\ \text{quantum states}}} P_j ln P_j + constant$$

or

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

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, namely n_j/N, where n_j is the number of molecules occupying molecular quantum state "j", and $Nk_B = n(N_Ak_B) = nR$.

As you will see later, this result is just the "entropy of mixing", namely, the disorder associated with mixing different kinds of molecules, for example, "red" molecules with "blue" molecules. Thus, for a system of N (N → NA) non-interacting identical particles, often referred to as a perfect gas, where the <u>molecular</u> energy

levels and molecular quantum states are well defined, the statistical entropy is simply the entropy of mixing associated with having molecules occupying different molecular quantum states!

• Effect of Temperature and Volume on Entropy – A Molecular Interpretation.

Recall entropy is a state function, a property of the system inasmuch as it offers a measure of the disorder or randomness of the system. Accordingly, we expect S to be a function of E_{system} and V, or T and V. We now illustrate this by way of a simple example.

Increasing E_{system} or T

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

$$\varepsilon_{nlm} = \frac{\hbar^2\left(n^2+m^2+l^2\right)\pi^2}{8mL^2}$$

n, m, l
are positive
integers

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 wavefunctions 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,

***n=1, m=1, l=1* for all molecules,**

then

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

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

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:

$$\phi_{211}(x_1,y_1,z_1) \prod_{i\neq 1}^{N} \phi_{111}(x_i,y_i,z_i)$$

$$\phi_{121}(x_1,y_1,z_1) \prod_{i\neq 1}^{N} \phi_{111}(x_i,y_i,z_i)$$

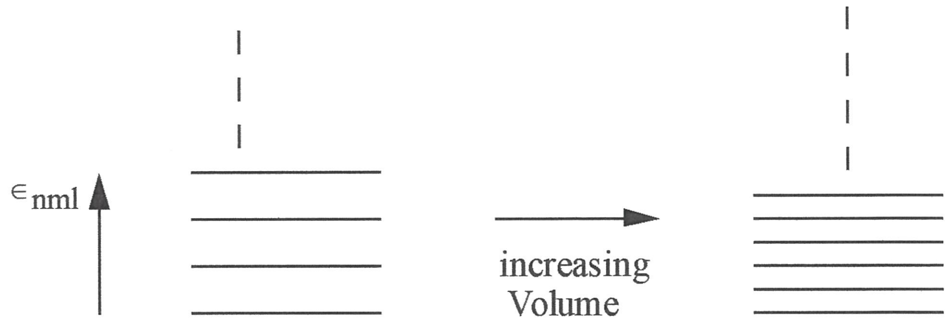
$$\phi_{112}(x_1,y_1,z_1) \prod_{i\neq 1}^{N} \phi_{111}(x_i,y_i,z_i)$$

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

Thus, the entropy of system has increased with increasing E_{system} or T. Accordingly, there is more

- **disorder**
- **randomness.**
- **Chao**

Increasing V



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

$$\Omega = aV^N$$

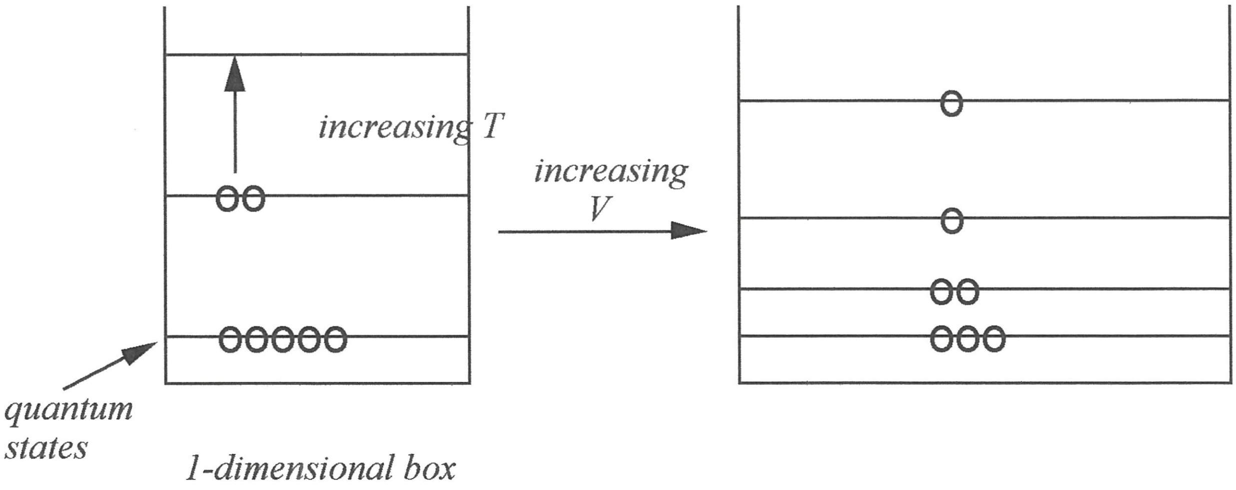
so that $\Delta S(V_1 \rightarrow V_2) = k_B ln\frac{\Omega_2}{\Omega_1}$

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

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

a result that we shall show again later.

Summary



Summary

Temperature: Increasing the 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}'s for the system. Therefore, the entropy of the system increases.

Volume: Increasing the volume will lower the energy of the translational energy states, making more quantum states accessible to molecules at a given temperature. The molecular energy levels become more closely packed. Again, the system degeneracy will go up.

• Distinguishable Molecules

So far, we have discussed N identical non-interacting particles that are indistinguishable, except that they occupy different molecular quantum states. If molecules of different chemical structure, isotopic composition, "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 the entropy of the initial and final states!

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

Second Law of Thermodynamics. Thermodynamic Entropy

- There are a number of different statements of the Second Law.

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

For reversible process: $dS = \frac{dQ_{rev}}{T}$

For irreversible process: $dS > \frac{dQ_{irrev}}{T}$

Here S is the thermodynamic entropy; 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.

In this course and in this lecture, we shall only be concerned with Statement (1) of the Second Law, namely,

For reversible process: $dS = \frac{dQ_{rev}}{T}$

For irreversible process: $dS > \frac{dQ_{irrev}}{T}$

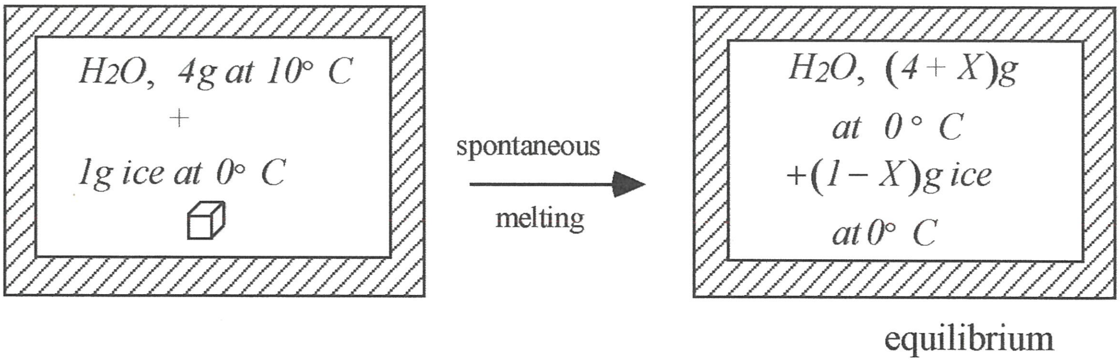
or $dS \geq \frac{dQ}{T}$

where dQ_{rev}, dQ_{irrev} denote heat input to system in a reversible and irreversible process respectively; and T is the absolute temperature of the system.

Note that we must write one expression for each subsystem of an otherwise isolated system, or an expression for the system and its surrounding if the system is not isolated.

We shall now discuss the implications of the Second Law by way of two illustrations.

- **A concrete example involving heat transfer only**



ΔE process = 0 ΔS process = ?

Equilibrium

How many grams of ice must melt to reach equilibrium?

Specific heat of water= 1 cal g^{-1} °C^{-1}
ΔH_{fusion} = 80 cal g^{-1}

To attain equilibrium, must melt x grams of ice to cool 4 grams of H_2O from 10 °C to 0 °C.

$$\text{or } (X\ g)(80\ \text{cal g}^{-1}) = (4g)(1\ \text{cal g}^{-1}\ {}^\circ C^{-1})(10^\circ C)$$

$80X = 40$ $X = 0.5g$

So process is

$$\begin{array}{c} H_2O,\ 4 \text{ grams at } 10^\circ C \\ + \\ 1 \text{ gram ice at } 0^\circ C \end{array} \longrightarrow \begin{array}{c} H_2O,\ (4.5) \text{ grams} \\ \text{at } 0^\circ C \\ +0.5 \text{ gram ice at } 0^\circ C \end{array}$$

$\underline{\Delta S_{process} = ?}$

$$\Delta S_{ice} = \int \frac{dQ_{rev}}{T_{ice}} \quad \overset{melting}{\underset{constant\ T}{\Rightarrow}} \quad \frac{Q_{rev}}{T_{ice}} = \frac{0.5g\ 80\ cal\ g^{-1}}{273K}$$

$$= 0.1465\ cal\ K^{-1}$$

$$\Delta S_{H_2O} = \int \frac{dQ_{rev}}{T_{water}} = \int_{283}^{273} \frac{CdT}{T_{water}} = 4g.\ \ 1\ cal\ g^{-1}\ {}^\circ C^{-1} \int_{283}^{273} \frac{dT}{T_{water}}$$

$$= 4 ln\left(\frac{273}{283}\right) cal\ K^{-1} = -0.1439\ cal\ K^{-1}$$

$$\begin{aligned} \Delta S_{process} &= \Delta S_{ice} + \Delta S_{H_2O} \\ &= (0.1465 - 0.1439)\ \text{cal K}^{-1} \\ &= 0.0026\ \text{cal K}^{-1} \\ &= (0.0026)\ (4.184\ \text{J K}^{-1}) \\ &= 0.0109\ \text{J K}^{-1} \end{aligned}$$

$1\ \text{kcal mol}^{-1}$	=	$4.184\ \text{kJ mol}^{-1}$
1 kcal	=	4.184 kJ
1 cal	=	4.184 J

Bottom line:

- $\Delta S_{\text{process}} = \Delta S_{\text{ice}} + \Delta S_{H_2O} \quad > \quad 0$

- $\Delta S_{\text{entire system (ice + water)}} \quad > \quad 0$

- **Overall process in the isolated system is spontaneous!!!**

- **Heat is transferred from a higher temperature to a lower temperature!!**

- **Second example: Entropy changes due to change in volume**

Consider perfect gas and reversible isothermal expansion.

Recall **First Law:** $dE = dQ - P_{ext}dV$

Reversible process $\Rightarrow$ $dE = dQ_{rev} - P_{system}dV$

$$= TdS - PdV$$

Isothermal expansion of ideal gas $\Rightarrow$ dE = 0
E(T) only

Therefore $TdS = PdV = \frac{nRT}{V}\,dV$

or $dS = \frac{nR}{V}\,dV$

$$\Delta S = \int_{V_i}^{V_f} \frac{nR}{V}\,dV = nRln\frac{V_f}{V_i}$$

Bottom line:

- **Entropy of perfect or ideal gas increases with an isothermal volume increase.**

Entropy of Mixing

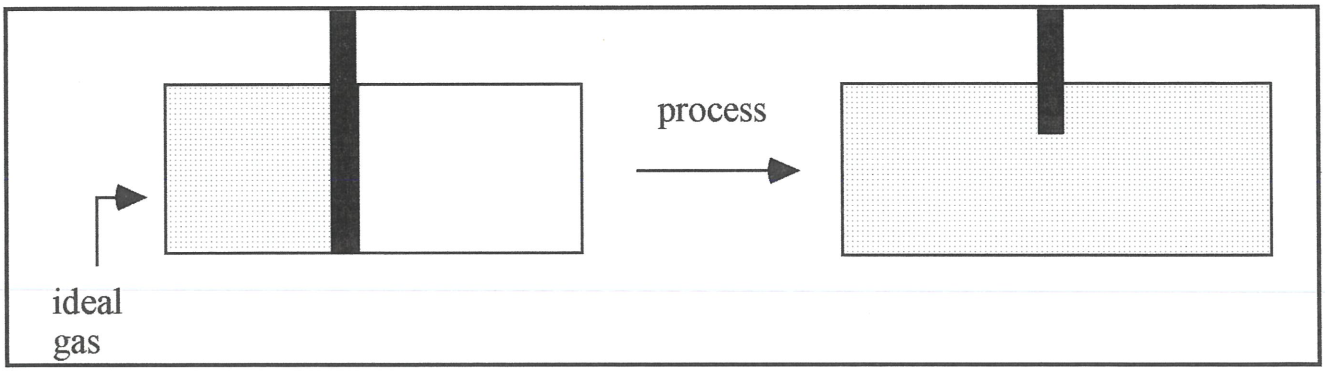
First, consider a pure substance (perfect gas).

S(N,T,V) or S(n,T,V)
S is a state function

Constant mass (closed) system, $S(T,V)$

Convenient independent variables

So it is simple to calculate ΔS for the following process based on the result that we have obtained.



N_i, T, V_i $(or\ n_i)$ ↑

volume accessible to gas molecules

$N_f,\ T,\ V_f$ $or\ (n_f)$

$$n_f = n_i \qquad = n$$

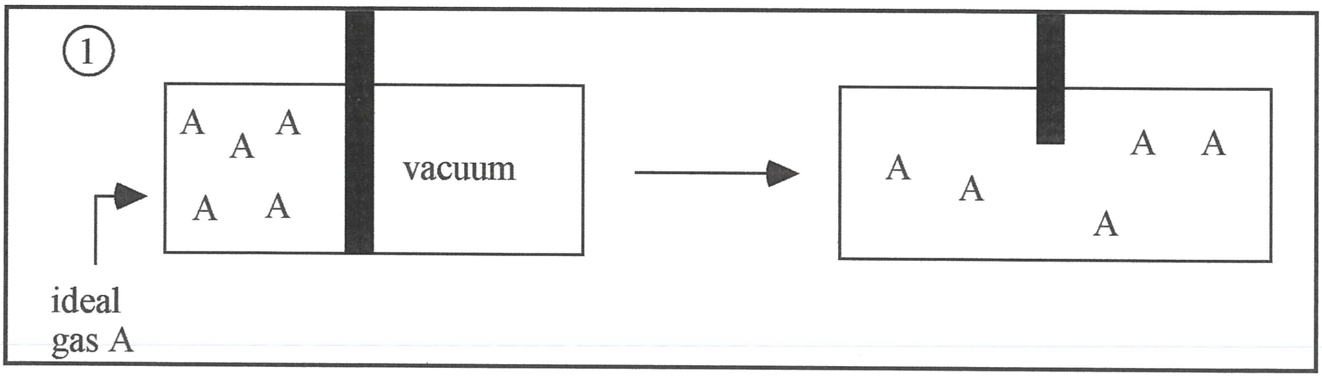
$$\therefore \Delta S_{process} = nR\ln\frac{V_f}{V_i}$$

depends on initial
and final states only

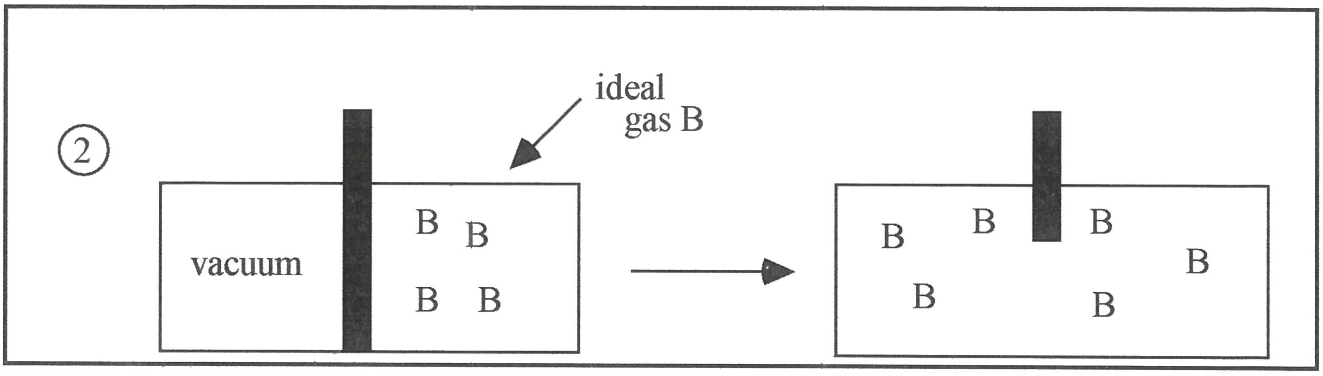
S is a state function!

What happens when a different gas at the same pressure initially occupies the two sides of the chamber?

Process is equivalent to sum of following two sub-processes.



n_A,	n_A
V_i^A	$V_f = V_T$
$T_i = T$	$T_f = T$
$P_i^A = \dfrac{n_A RT}{V_i^A}$	$P_f^A = \dfrac{n_A RT}{V_T}$



Volume or phase space accessible to each of the gases per mole has increased!!

$$n_B \qquad V_i^B \qquad T_i = T \qquad P_i^B = \frac{n_B RT}{V_i^B}$$

$$n_B \qquad V_f = V_T \qquad T_f = T \qquad P_f^B = \frac{n_B RT}{V_T}$$

$$\Delta S process = \Delta S_A + \Delta S_B$$

$$= n_A R ln\left(\frac{V_T}{V_i^A}\right)\left(\cancel{\frac{n_A}{n_A}}\right) + n_B R ln\left(\frac{V_T}{V_i^B}\right)\left(\cancel{\frac{n_B}{n_B}}\right)$$

Initial pressures same $\Rightarrow$ $\dfrac{n_A}{V_i^A} = \dfrac{n_B}{V_i^B}$

Final pressure

same

$$P_f = P_f^A + P_f^B = \frac{n_A RT}{V_T} + \frac{n_B RT}{V_T} = \left[\left(\frac{n_A}{V_i^A}\right)\frac{V_i^A}{V_T} + \left(\frac{n_B}{V_i^B}\right)\frac{V_i^B}{V_T}\right]RT.$$

$$= \frac{n_A}{V_i^A}\frac{(V_i^A + V_i^B)}{V_T}.RT = \frac{n_A}{V_i^A}.RT = P_i^A = P_i^B$$

So $$\frac{n_A + n_B}{V_T} = \frac{n_A}{V_i^A} = \frac{n_B}{V_i^B}$$

or $$\boxed{\begin{aligned} \frac{V_T}{V_i^A} &= \frac{n_A + n_B}{n_A} = X_A^{-1} \\ \text{and} \quad \frac{V_T}{V_i^B} &= \frac{n_A + n_B}{n_B} = X_B^{-1} \end{aligned}}$$

$$\therefore \; \Delta S_{process} = -n_A R \ln X_A - n_B R \ln X_B$$

$$= -n_T \left[X_A R \ln X_A + X_B R \ln X_B \right]$$

entropy of mixing!

General Formula for Entropy of Mixing of Ideal Solutions (gases, liquids, or solids)

$$\boxed{\Delta S_{mixing} = -n_T R \sum_i X_i \ln X_i}$$

(if per mole of mixture, $n_T = 1$)

components
in mixture

Entropy Changes in General

Recall, for complex systems, e.g., a chemical system or a biological cell, we must appeal to the general results derived from thermodynamics to determine ΔE, ΔH, and ΔS for a process. In practice, we need to determine ΔE, ΔH, and ΔS not only for the system itself, but also for its surroundings, and add the changes for both the system and the surroundings.

The important result of the Second Law is that

$$\Delta S_{\text{process}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

$\Delta S_{\text{process}} > 0$ **if the process is spontaneous**

$\Delta S_{\text{process}} = 0$ **if the system is already in equilibrium with its surroundings.**

So one typically includes ΔS_{system} and $\Delta S_{\text{surroundings}}$ in the analysis of the problem.

Now, for each part (i.e., system or surroundings), we can take advantage that $S \equiv$ thermodynamic entropy is a state function; i.e., $S(n,T,V)$ *or* $S(n,T,P)$, and we can appeal to the First Law to derive some general results, that are completely general for simple as well as the most complex systems. For example,

according to the First Law, we can write

$$dE = dQ - P_{ext}dV \qquad (\text{general})$$

$$dE = dQ_{rev} - PdV \qquad (\text{reversible})$$

$$\boxed{dE = TdS - PdV} \quad \text{general}$$

$$\text{or} \quad dS = \frac{dE + PdV}{T}$$

Since we may express further, e.g.

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

$$= C_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

we have $$\boxed{dS = \frac{C_V}{T} dT + \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] dV}$$ completely general!

In general, one would write one equation for the system and one for the surroundings, or each subsystem of an otherwise isolated system.

<u>Examples</u>

- **For an ideal or perfect gas**

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \;\;\&\;\; P = \frac{nRT}{V}, \;\; so \;\; \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] = \frac{nR}{V}$$

$$\therefore dS = \frac{C_V}{T} dT + \frac{nR}{V} dV \qquad \text{(ideal gas)}$$

and $$\Delta S_{ideal\ gas} = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$= C_V \ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{V_f}{V_i}\right)$$

- **For constant pressure processes, more convenient to recast above in terms of enthalpy H**

$dE = TdS - pdV$ general

Now $dH = dE + pdV + VdP$ general

Combining, we have $dH = TdS + Vdp$

Since we may express dH further, e.g.

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\boxed{dS = \frac{C_P}{T} dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP}$$

For a constant pressure process, then

$$\Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT$$

Note that if phase changes take place during process, there exist singularities in C_p, but

$$\Delta S_{phase\ transition} = \frac{1}{T_{transition}} \int_{transition} C_P\, dT = \frac{\Delta H_{transition}}{T_{transition}}$$

- **Cyclic processes**

For system that has undergone a complete cycle,

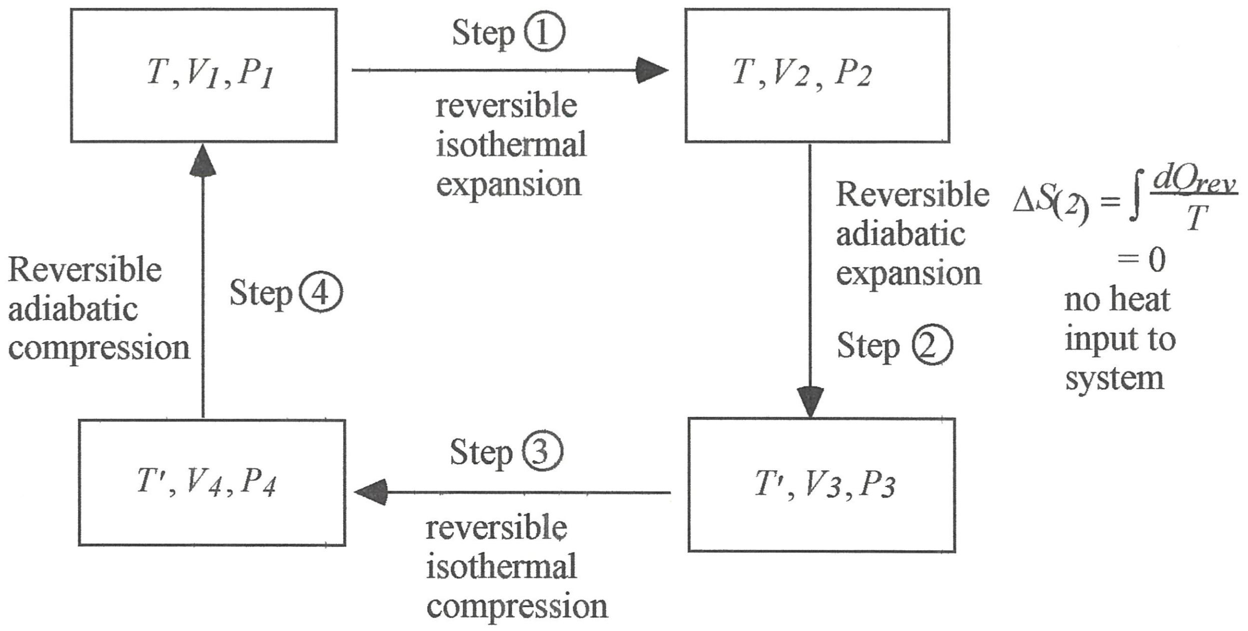
$\Delta S_{system} = 0$ since $\oint dS = 0$ & S is a state function.

but $\Delta S_{system} + \Delta S_{surroundings} = \oint d_{system} + \Delta S_{surrounding}$

≥ 0 *depending upon whether the process is reversible or irreversible*

or $\oint dS_{system\ +\ surrounding} \geq 0$

Example of a cyclic process



		$\Delta S_{step}{}^{system}$
Step 1	Reversible isothermal expansion	$nR\ln\left(\frac{V_2}{V_1}\right)$
Step 2	Reversible adiabatic expansion	0
Step 3	Reversible isothermal compression	$nR\ln\left(\frac{V_4}{V_3}\right)$
Step 4	Reversible adiabatic compression	0

$$\Delta S_{\substack{gas \\ system}} = nR\ln\left(\frac{V_2}{V_1}\right) + nR\ln\left(\frac{V_4}{V_3}\right)$$

<u>Need</u> $\frac{V_2}{V_1}$ *and* $\frac{V_4}{V_3}$

From step 2, adiabatic reversible expansion

$$\left(\frac{T'}{T}\right) = \left(\frac{V_2}{V_3}\right)^{nR/C_V}$$

From step 4, adiabatic reversible compression

$$\left(\frac{T}{T'}\right) = \left(\frac{V_4}{V_1}\right)^{nR/C_V}$$

or $\frac{V_2}{V_3} = \frac{V_1}{V_4}$

or $\frac{V_2}{V_1} = \frac{V_3}{V_4}$

$$\therefore \Delta S_{\substack{gas \\ system}} = nRln\left(\frac{V_2}{V_1}\right) - nRln\left(\frac{V_3}{V_4}\right) = 0$$

On the other hand,

$$Q_{system} = Q_{step\ 1} + Q_{step\ 2} + Q_{step\ 3} + Q_{step\ 4}$$

$$= nRTln\left(\frac{V_2}{V_1}\right) + 0 + nRT'ln\left(\frac{V_4}{V_3}\right) + 0$$

$$= nRTln\left(\frac{V_2}{V_1}\right) + nRT'ln\left(\frac{V_4}{V_3}\right) \qquad \neq 0$$

This result probably prompted Clausius to introduce S and $dS = \frac{dQ_{rev}}{T}$.

Third Law of Thermodynamics

The entropy of a perfectly ordered material, such as a perfect crystal or a perfect superfluid such as liquid helium, approaches zero as the temperature approaches absolute zero.

$$\lim_{T \to 0K} S = 0 \quad \text{for a perfectly ordered material}$$

Why we need the Second Law!

Next time, we will discuss why we need the Second Law. We will also introduce the concept of Free Energy.