

Thermodynamics of Materials

9th Lecture
2008. 3. 31 (Mon.)

A rigid container is divided into two compartments of equal volume by a partition. One compartment contains 1 mole of ideal gas A at 1 atm, and the other contains 1 mole of ideal gas B at 1 atm.

Calculate the increase in entropy which occurs when the partition between the two compartments is removed.

| | |
|-----------------------|-----------------------|
| 1 mol (1 atm) A | 1 mol (1 atm) B |
|-----------------------|-----------------------|

Calculate the increase in entropy

- 1) by Boltzmann's way
- 2) by volume change of each gas
- 3) by pressure change of each gas

볼츠만 엔트로피로 구하는 법

| | |
|-----------------------|-----------------------|
| 1 mol (1 atm) A | 1 mol (1 atm) B |
|-----------------------|-----------------------|

$$P_1 = \left(\frac{1}{2}\right)^N \left(\frac{1}{2}\right)^N$$

$$P_2 = 1$$

$$\begin{aligned}\Delta S_{1 \rightarrow 2} &= S_2 - S_1 \\ &= k \ln P_2 - k \ln P_1 \\ &= k \ln \left(\frac{P_2}{P_1} \right) = k \ln 2^N 2^N = k \ln 2^N + k \ln 2^N \\ &= R \ln 2 + R \ln 2 = 2R \ln 2 = R \ln 4\end{aligned}$$

Volume 변화로 생각해서 구하는 법

| | |
|-----------------------|-----------------------|
| 1 mol (1 atm) A | 1 mol (1 atm) B |
|-----------------------|-----------------------|

Isothermal mixing
→ No change in E

$$dE = 0 = \delta q - \delta w \quad \delta q = \delta w = PdV$$

$$\Delta S_A = \int \frac{\delta q}{T} = \int \frac{P}{T} dV \quad PV = RT \rightarrow \frac{P}{T} = \frac{R}{V}$$

$$= \int \frac{R}{V} dV = R \ln \frac{V_2}{V_1} = R \ln 2$$

$$\Delta S_B = \int \frac{\delta q}{T} = \int \frac{P}{T} dV = \int \frac{R}{V} dV = R \ln \frac{V_2}{V_1} = R \ln 2$$

$$\therefore \Delta S = \Delta S_A + \Delta S_B = R \ln 4$$

Pressure 변화로 생각해서 구하는 법

| | |
|-----------------------|-----------------------|
| 1 mol (1 atm) A | 1 mol (1 atm) B |
|-----------------------|-----------------------|

Isothermal mixing
→ No change in E

$$\Delta S = \int \frac{\delta q}{T} = \int \frac{P}{T} dV = \int \frac{R}{V} dV = R \ln \frac{V_2}{V_1}$$

$$= R \ln \frac{P_1}{P_2} \quad (\because P_1 V_1 = P_2 V_2 \text{ at constant } T)$$

$$P_{A,1} = 1, P_{A,2} = 0.5$$

$$P_{B,1} = 1, P_{B,2} = 0.5$$

$$\Delta S_A = R \ln \frac{P_1}{P_2} = R \ln \frac{1}{0.5} = R \ln 2$$

$$\Delta S_B = R \ln \frac{P_1}{P_2} = R \ln \frac{1}{0.5} = R \ln 2$$

$$\therefore \Delta S = \Delta S_A + \Delta S_B = R \ln 4$$

If the first compartment has contained 2 moles of ideal gas A, what would have been the increase in entropy when the partition was removed?

Calculate the change in entropy in three ways (Boltzman, volume change, pressure change).

| | |
|-----------------------|-----------------------|
| 2 mol (2 atm) A | 1 mol (1 atm) B |
|-----------------------|-----------------------|

볼츠만 엔트로피로 구하는 법

| | |
|-----------------------|-----------------------|
| 2 mol (2 atm) A | 1 mol (1 atm) B |
|-----------------------|-----------------------|

$$P_1 = \left(\frac{1}{2}\right)^{2N} \left(\frac{1}{2}\right)^N \quad P_2 = 1$$

$$\Delta S_{1 \rightarrow 2} = S_2 - S_1 = kT \ln \frac{P_2}{P_1}$$

$$\Delta S_{1 \rightarrow 2} = k \ln(2)^{2N} (2)^N$$

$$= 3R \ln(2) = R \ln 8$$

$$\therefore \Delta S_{1 \rightarrow 2} = R \ln 8$$

Volume 변화로 생각해서 구하는 법

| | | |
|-----------------------|-----------------------|----------------------------------------------|
| 2 mol (2 atm) A | 1 mol (1 atm) B | Isothermal mixing → No change in E |
| | | |

$$dE = 0 = \delta q - \delta w \quad \delta q = \delta w = PdV$$

$$\delta q = \delta w = PdV = \frac{nRT}{V} dV = nRT \ln \frac{V_2}{V_1}$$

$$\Delta S_A = 2R \ln \frac{V_2}{V_1} = 2R \ln \frac{2V_1}{V_1} = 2R \ln 2$$

$$\Delta S_B = R \ln \frac{V_2}{V_1} = R \ln 2$$

$$\therefore \Delta S = \Delta S_A + \Delta S_B = 3R \ln 2 = R \ln 8$$

Pressure 변화로 생각해서 구하는 법

| | | |
|-----------------------|-----------------------|----------------------------------------------|
| 2 mol (2 atm) A | 1 mol (1 atm) B | Isothermal mixing → No change in E |
| | | |

$$\delta q = \delta w = PdV = \frac{nRT}{V} dV = nRT \ln \frac{V_2}{V_1} \quad \begin{matrix} P_{A,1} = 2, P_{A,2} = 1 \\ P_{B,1} = 1, P_{B,2} = 0.5 \end{matrix}$$

$$T \text{가 일정할 때 } P_1 V_1 = P_2 V_2 \rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

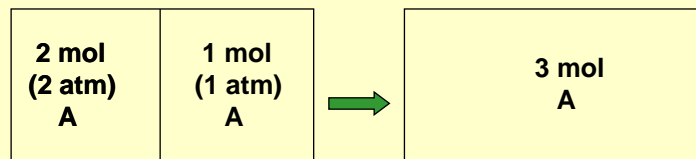
$$\Delta S_A = 2R \ln \frac{V_2}{V_1} = 2R \ln \frac{P_1}{P_2} = 2R \ln \frac{2}{1} = 2R \ln 2$$

$$\Delta S_B = R \ln \frac{P_1}{P_2} = R \ln \frac{1}{0.5} = R \ln 2$$

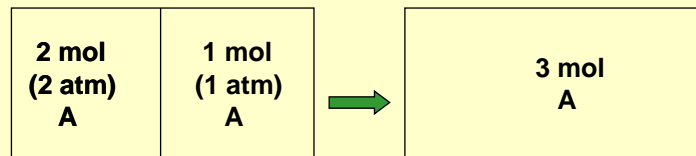
$$\therefore \Delta S = \Delta S_A + \Delta S_B = 3R \ln 2$$

Calculate the corresponding increase in entropy in each of the above two situations if both compartments had contained ideal gas A.

Calculate the change in entropy in three ways (Boltzman, Volume Change, Pressure Change).



볼츠만 엔트로피로 구하는 법



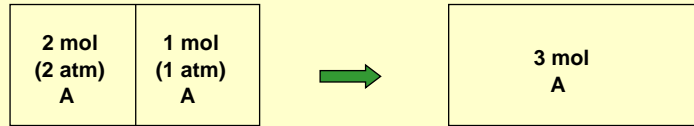
$$P_1 = {}_{3N}C_{2N} \left(\frac{1}{2}\right)^{2N} \left(\frac{1}{2}\right)^N \quad P_2 = 1$$

$$\Delta S_{1 \rightarrow 2} = k \ln \frac{P_2}{P_1} = k \ln \frac{2^{2N} 2^N}{{}_{3N}C_{2N}} = R \ln \frac{8}{{}_{3N}C_{2N}} \quad {}_{3N}C_{2N} = \frac{3N!}{2N!N!}$$

$$\begin{aligned} \ln({}_{3N}C_{2N}) &= 3N \ln 3N - 3N \\ &\quad - (2N \ln 2N - 2N + N \ln N - N) \\ &= 3N \ln 3 - 2N \ln 2 = R \ln \frac{27}{4} \end{aligned}$$

$$\therefore \Delta S_{1 \rightarrow 2} = R \ln \frac{32}{27}$$

Volume 변화로 생각해서 구하는 법



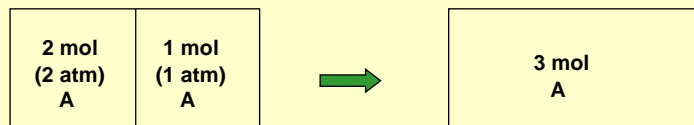
$$V_{A,1} = \frac{1}{2}, V_{A,2} = \frac{2}{3} \quad (3\text{몰이 } 2\text{개의 부피} \rightarrow 1\text{몰은 } \frac{2}{3}\text{부피})$$

$$V_{A',1} = 1, V_{A',2} = \frac{2}{3} \quad (1\text{몰은 } \frac{2}{3}\text{부피에 해당} \rightarrow \frac{2}{3})$$

$$\Delta S_A = 2R \ln \frac{V_2}{V_1} = 2R \ln \frac{4}{3} \quad \Delta S_{A'} = R \ln \frac{V_2}{V_1} = R \ln \frac{2}{3}$$

$$\therefore \Delta S = \Delta S_A + \Delta S_{A'} = R \ln \frac{32}{27}$$

Pressure 변화로 생각해서 구하는 법



$$P_{A,1} = \frac{2}{V_1} RT, \quad P_{A,2} = \frac{3}{2V_1} RT \quad \Rightarrow \quad \frac{P_1}{P_2} = \frac{4}{3}$$

$$P_{A',1} = \frac{1}{V_1} RT, \quad P_{A',2} = \frac{3}{2V_1} RT \quad \Rightarrow \quad \frac{P_1}{P_2} = \frac{2}{3}$$

$$\Delta S_A = 2R \ln \frac{P_1}{P_2} = 2R \ln \frac{4}{3} \quad \Delta S_{A'} = R \ln \frac{P_1}{P_2} = R \ln \frac{2}{3}$$

$$\therefore \Delta S = \Delta S_A + \Delta S_{A'} = R \ln \frac{32}{27}$$

Statistical Thermodynamics

(D.R. Gaskell Chap. 4 and R.T. DeHoff, Chap. 6)

Atomic description of thermodynamics in contrast with phenomenological description

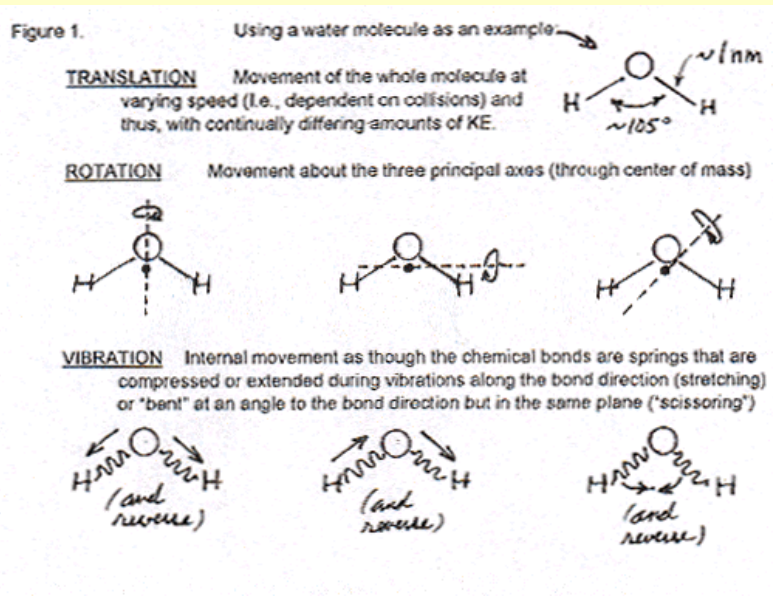
microstate vs macrostate

Fundamental assumption or principle in ST

→ All microstates are equally probable.

→ The probability of occurrence of any given macrostate (n_j), which is macroscopically observable phenomenon, is proportional to the number of possible microstates.

A postulate of the quantum theory is that, if a particle is confined to move within a given fixed volume, then **its energy is quantized**, i.e., the particle may only have certain **discrete allowed values of energy**, which are separated by **“forbidden energy bands.”**

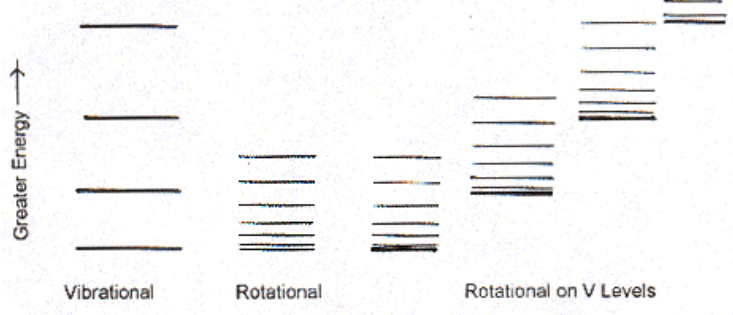


<http://www.2ndlaw.com/entropy.html>

Quantized Energy → Energy Levels

Figure 2. Schematic of vibrational (V) and rotational (R) energy levels for complex molecules (Molecules more complex than water can have varied conformations, allowing more V and R modes.) Each V level has an R level that may overlap the next higher V level. Therefore, showing a complete schematic is confusing. The staggered diagram at the right should be "slid together" horizontally for a semi-realistic depiction.

The conclusion that can be drawn from this schematic is important: When more energy is put into a system, its molecules can occupy a great many additional energy levels – higher energy V levels that each can have many R levels (and of course every R level has translational levels within it).



<http://www.2ndlaw.com/entropy.html>

Equilibrium

The most probable distribution of molecules on various accessible energy levels

The maximum number of microstates

one mole = 6×10^{23} molecules

Microstate

One arrangement in which the total energy of the system is distributed among energy levels and in space.

Irreversibility

→ change from less number of microstates to more number of microstates.

W = number of microstates

S = k ln W

$$\begin{aligned}\Delta S_{1 \rightarrow 2} &= S_2 - S_1 = k \ln W_2 - k \ln W_1 \\ &= k \ln \frac{W_2}{W_1}\end{aligned}$$

$$\Delta S_{1 \rightarrow 2} = k \ln \left(\frac{\text{no. of microstates}_2}{\text{no. of microstates}_1} \right)$$

***How many microstates are there
in one mole of ice or water at 273 K?***

*How many microstates are there
in one mole of ice or water at 273 K?*

Hint)

$$\Delta S_{273K} \text{ for ice} = 41 \text{ J/K}$$

$$\Delta S_{273K} \text{ for water} = 63 \text{ J/K}$$

$$\Delta S_{0 \rightarrow 273K} = k \ln \frac{W_{273K}}{W_{0K}} = k \ln \frac{W_{273K}}{1} = k \ln W_{273K}$$

$$\Delta S_{0 \rightarrow 273K} \text{ for ice} = 41 \text{ J/K}$$

$$41 \text{ J/K} = k \ln W_{273K} = 1.4 \times 10^{-23} \ln W_{273K}$$

$$\rightarrow \ln W_{273K} = 2.9 \times 10^{24}$$

$$\rightarrow W_{273K} = e^{2.9 \times 10^{24}} = 10^{1.3 \times 10^{24}}$$

\rightarrow *number of microstates
for one mole of ice*

$$\Delta S_{0 \rightarrow 273K} \text{ for water} = 63 \text{ J / K}$$

$$63 \text{ J / K} = k \ln W_{273K} = 1.4 \times 10^{-23} \ln W_{273K}$$

$$\rightarrow W_{273K} = 10^{2.0 \times 10^{24}}$$

→ number of microstates
for one mole of water

$$\text{cf. } W_{273K}^{\text{ice}} = 10^{1.3 \times 10^{24}}$$

Colligative Effects (비점상승, 융점강하)

*The solution's entropy is greater than that of the pure solvent because solution has a higher **density of states**.*

*Solvent molecules less tend to "escape" from their **greater entropy state** in the solution to a vapor phase or to a solid phase than they "escape" from the pure solvent.*

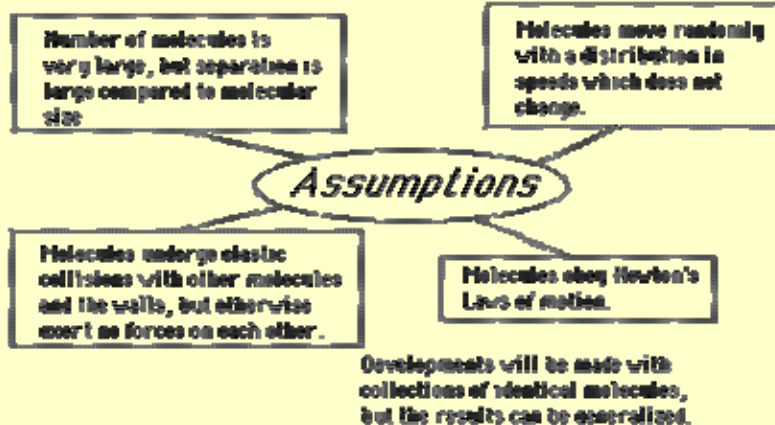
This lessened tendency to leave the solution results in a higher boiling point and lower freezing point for the solution compared to the pure solvent.

<http://www.2ndlaw.com/entropy.html>

Atomistic View

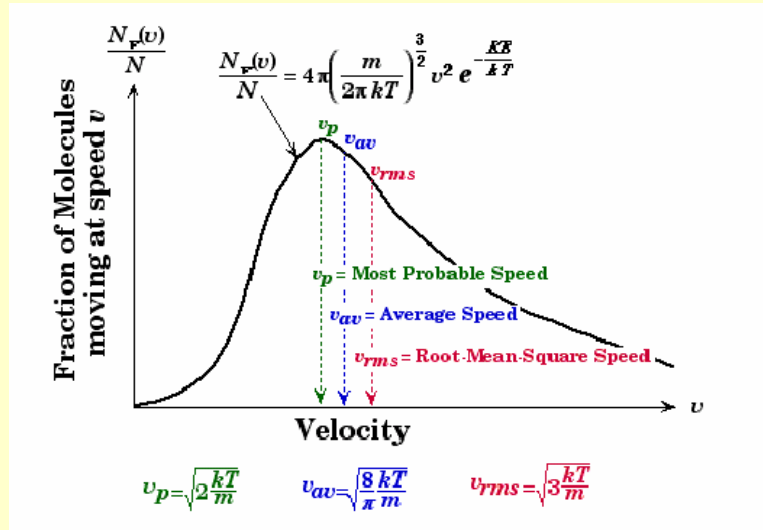
- *What is pressure?*
- *What is temperature?*
- *What is internal energy?*
- *What is heat or heat capacity?*
- *What is entropy?*

Kinetic Theory



<http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html>

Maxwell-Boltzmann Velocity Distribution of Gas



Newton's Laws and Collisions

For N identical molecules:

For N molecules:

$$\bar{F} = \frac{m [v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \dots + v_{Nx}^2]}{L}$$

but this can be related to the average:

$$\bar{v}_x^2 = \frac{v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \dots + v_{Nx}^2}{N}$$

Force of molecular collision with wall

$$\bar{F} \Delta t = \Delta p = 2mv_x$$

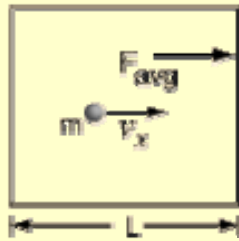
The time for a "round trip" is $\Delta t = \frac{2L}{v_x}$

so the average force is $\bar{F} = \frac{2mv_x}{2L} = \frac{mv_x^2}{L}$

and for N molecules: $\bar{F} = \frac{mN\bar{v}_x^2}{L}$

Before: v_x → | Perfectly elastic collision with wall
 After: ← v_x

What is Gas Pressure?



$$F_{average} = \frac{mNv_x^2}{L}$$

$$v^2 = v_x^2 + v_y^2 + v_z^2 = 3v_x^2$$

$$P = \frac{F_{avg}}{A} = \frac{mNv^2}{3LA} = \frac{mNv^2}{3V} = \frac{N}{3V}mv^2$$

$$P = \frac{2N}{3V} \left[\frac{1}{2}mv^2 \right]$$

$$\left[\frac{1}{2}mv^2 \right] = \frac{3}{2}kT$$

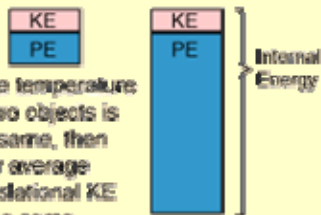
$$P = \frac{2N}{3V} \cdot \frac{3}{2}kT = \frac{kN}{V}T = \frac{RT}{V}$$

$$PV = RT$$

<http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html>

What is Temperature?

→ translational K.E.



If the temperature of two objects is the same, then their average translational KE is the same.

Their internal energies and specific heats will not necessarily be the same.

$$\left[\frac{1}{2}mv^2 \right]_{average} = \frac{3}{2}kT$$

defines the kinetic temperature

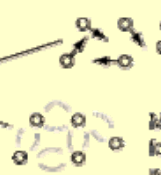
k = Boltzmann constant

<http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html>

What is Internal Energy?

Does a glass of water sitting on a table have any energy?

No apparent energy of the glass of water on a macroscopic scale.



Microscopic kinetic energy is part of internal energy.

Molecular attractive forces are associated with potential energy

<http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html>

What is Heat Capacity?

→ *capacity to store energy (heat)*

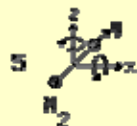
Degree
of
freedom



Monoatomic

$$C_V = \frac{3}{2} R = 12.5 \frac{\text{J}}{\text{mol K}}$$

Helium 12.5
Argon 12.6



Diatomic

$$C_V = \frac{5}{2} R = 20.8 \frac{\text{J}}{\text{mol K}}$$

Nitrogen (N₂) 20.7
Oxygen (O₂) 20.8

$$C_V = 7/2 R$$



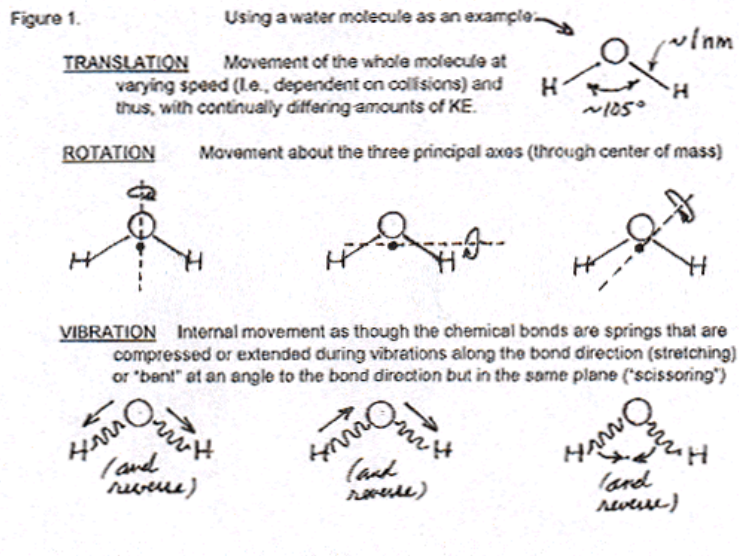
Polyatomic

$$C_V = \frac{6}{2} R = 24.9 \frac{\text{J}}{\text{mol K}}$$

Ammonia (NH₃) 29.0
Carbon dioxide (CO₂) 29.7

$$C_V > 7/2 R$$

<http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html>



<http://www.2ndlaw.com/entropy.html>

단원자 기체 : *translation*

다원자 기체 : *translation, rotation, vibration*

액체 : *translation, rotation, vibration*

고체 : *constrained vibration*

vibration frequency $\cong 10^{12}/\text{sec}$

→ 물질이 에너지를 저장하는 방법

**Vibration : large energy difference
between levels**

→ difficult to be excited.

→ high E levels are not accessible.

Most liquid water molecules and gas phase water
are in the lowest vibrational state.

**Rotation : small energy difference
between levels**

→ easy to be excited

Water molecules rotate faster and faster
with increasing temperature.

**Translation : very small energy difference
between levels**

→ very easily excited

그림에서 첫번째 **rotation level** 근처

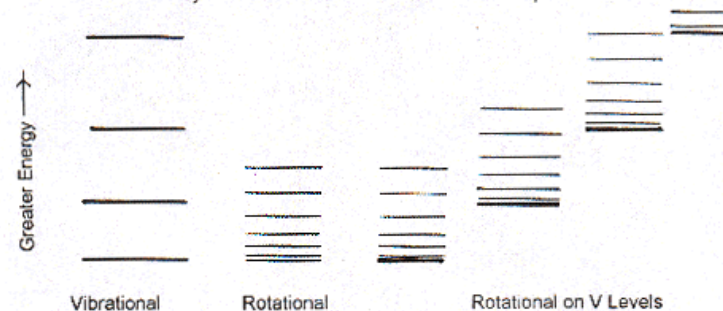
At RT, ~ 1000 miles an hour

Quantized Energy → Energy Levels

Figure 2. Schematic of vibrational (V) and rotational (R) energy levels for complex molecules
(Molecules more complex than water can have varied conformations, allowing more V and R modes.)

Each V level has an R level that may overlap the next higher V level. Therefore, showing a complete schematic is confusing. The staggered diagram at the right should be "slid together" horizontally for a semi-realistic depiction.

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Energy Difference between the Ground State and the First excited State

(CO at 300K in a box 10 cm on a side)

- *Average thermal energy, $kT = 0.59$ kcal/mole*
- *Translational energy, $\Delta E_t = 1.7 \times 10^{-20}$ kcal/mole*
- *Rotational energy, $\Delta E_r = 0.01104$ kcal/mole*
- *Vibrational energy, $\Delta E_v = 6.21$ kcal/mole*
- *Electronic energy, $\Delta E_e = 186.0$ kcal/mole*

Wavelengths to measure changes in the various modes of energy

(CO at 300K in a box 10 cm on a side)

| <i>Mode</i> | <i>Wavelength</i> | <i>Portion of spectrum</i> |
|-------------|-------------------|----------------------------|
|-------------|-------------------|----------------------------|

- | | |
|--------------------------------------------------------------------------|----------------------------|
| • <i>Translational energy, $\lambda_t = 0.2$ light years,</i> | <i>none</i> |
| • <i>Rotational energy, $\lambda_r = 0.26$ cm,</i> | <i>far IR or Microwave</i> |
| • <i>Vibration energy, $\lambda_v = 4,610 \mu,$</i> | <i>near IR</i> |
| • <i>Electronic energy, $\lambda_e = 0.154 \mu,$</i> | <i>UV</i> |