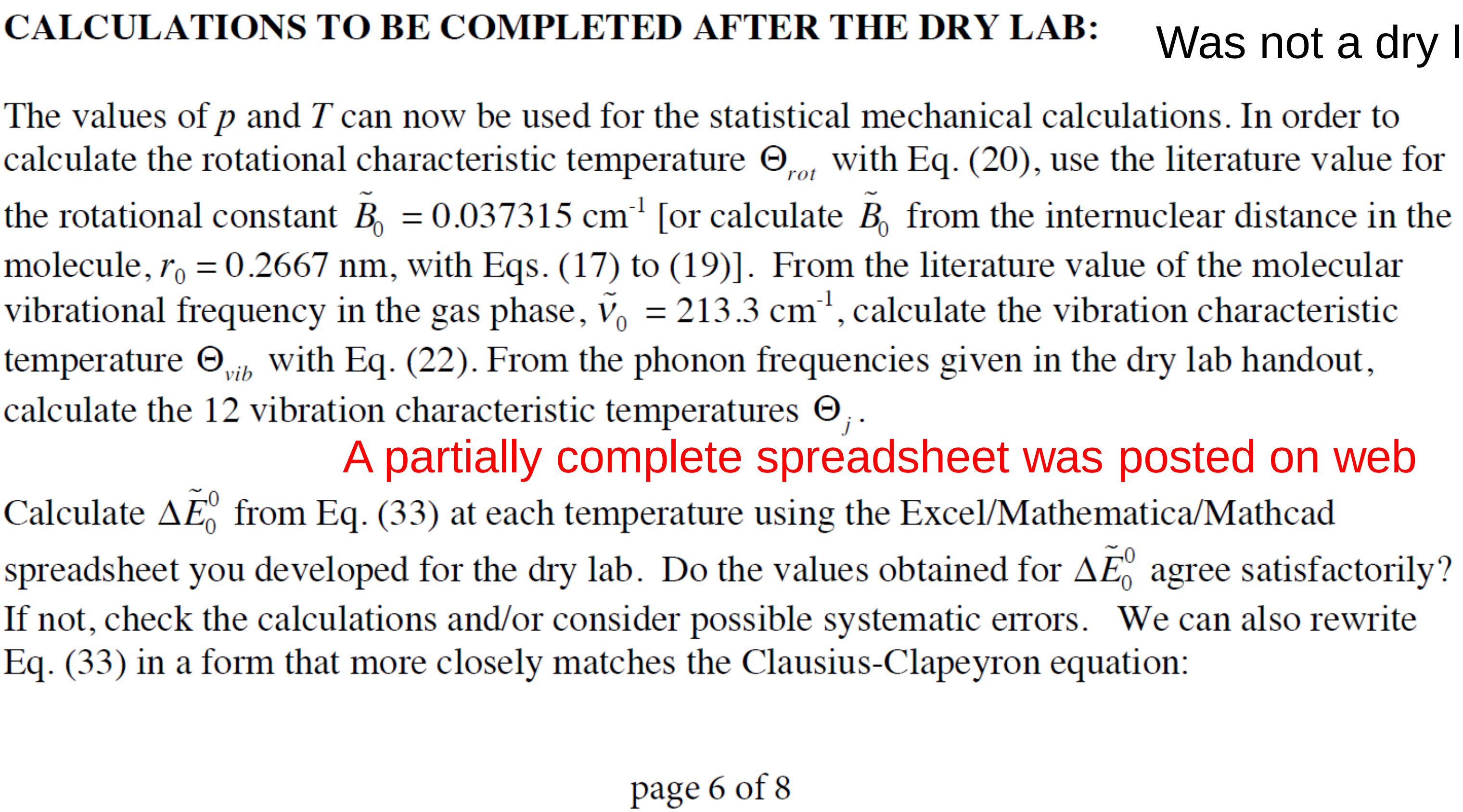
Prelab Lecture

Chmy 374 Thur., March 22, 2018

Edited 22mar18, 21mar18

LAB REPORT: From the ClassicalThermoI2Sub-17.pdf handout:



CALCULATIONS TO BE COMPLETED AFTER THE DRY LAB:

Was not a dry lab

The values of p and T can now be used for the statistical mechanical calculations. In order to calculate the rotational characteristic temperature Θ_{rot} with Eq. (20), use the literature value for the rotational constant $\tilde{B}_0 = 0.037315 \text{ cm}^{-1}$ [or calculate $\tilde{B}_0$ from the internuclear distance in the molecule, $r_0 = 0.2667$ nm, with Eqs. (17) to (19)]. From the literature value of the molecular vibrational frequency in the gas phase, $\tilde{\nu}_0 = 213.3 \text{ cm}^{-1}$, calculate the vibration characteristic temperature Θ_{vib} with Eq. (22). From the phonon frequencies given in the dry lab handout, calculate the 12 vibration characteristic temperatures Θ_j.

A partially complete spreadsheet was posted on web

Calculate $\Delta\tilde{E}_0^0$ from Eq. (33) at each temperature using the Excel/Mathematica/Mathcad spreadsheet you developed for the dry lab. Do the values obtained for $\Delta\tilde{E}_0^0$ agree satisfactorily? If not, check the calculations and/or consider possible systematic errors. We can also rewrite Eq. (33) in a form that more closely matches the Clausius-Clapeyron equation:

page 6 of 8

$$\ln p - \ln\left[\frac{T^{7/2}\prod_{j=1}^{12}(1-e^{-\Theta_j/T})^{1/2}}{(1-e^{-\Theta_{vib}/T})}\right] = \ln\left[\left(\frac{2\pi mk}{h^2}\right)^{3/2}\frac{k}{\sigma\Theta_{rot}}\right] - \frac{\Delta\tilde{E}_0^0}{RT} \tag{37}$$

Plot the LHS of Eq. (37) against $1/T$, and determine both $\Delta\tilde{E}_0^0$ and the constant term graphically or by least squares. Does this value of $\Delta\tilde{E}_0^0$ agree with the average of the values obtained by direct application of Eq. (37)? Does the constant term agree with the theoretical value?

Entropy and Enthalpy of Sublimation. Since we have a system of only one component, the chemical potentials for I_2 in crystalline and gaseous forms, given in Eqs. (32) and (25), respectively, are equivalent to the molar Gibbs free energies $\tilde{G}_s$ and $\tilde{G}_g$, aside from an additive constant. The entropies of the two phases can be obtained by differentiating with respect to temperature. The expressions obtained are

$$\begin{aligned}\tilde{S}_s &= -\left(\frac{\partial\tilde{G}_s}{\partial T}\right)_p = -\left(\frac{\partial\mu_s}{\partial T}\right)_p \\ &= \frac{R}{2}\sum_{j=1}^{12}\left[\frac{\Theta_j/T}{e^{\Theta_j/T}-1} - \ln(1-e^{-\Theta_j/T})\right]\end{aligned} \tag{38}$$

$$\begin{aligned}\tilde{S}_g &= -\left(\frac{\partial\tilde{G}_g}{\partial T}\right)_p = -\left(\frac{\partial\mu_g}{\partial T}\right)_p \\ &= \frac{\Delta\tilde{E}_0^0 - \mu_g}{T} + \frac{7}{2}R + R\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T}-1}\end{aligned} \tag{39}$$

The heat of sublimation at temperature T is

$$\Delta\tilde{H}_{sub} = T\Delta\tilde{S}_{sub} = T(\tilde{S}_g - \tilde{S}_s) \tag{40}$$

Calculate the molar entropies $\tilde{S}_s$ and $\tilde{S}_g$ of the crystalline and vapor forms of I_2 at 320 K with Eqs. (38) and (39), and obtain the molar heat of sublimation $\Delta\tilde{H}_{sub}$ with Eq. (40). Compare it with the value obtained by the Clausius-Clapeyron method and with any literature values that you can find.

DISCUSSION

Of the two methods of determining $\Delta\tilde{E}_0^0$ with Eqs. (33) and (37), which do you judge gives the more precise value? Which gives the more accurate value? Which provides the better test of the overall statistical mechanical approach? Compare this approach with the purely thermodynamic

method using the integrated Clausius-Clapeyron equation, taking into account the approximations involved in the latter. State the average temperature corresponding to your Clapeyron value of ΔH_{sub}.

Comment on the choice of representative values of $\tilde{\nu}_J$ for the 12 vibrational modes of the crystal. How much would reasonable changes (say, 10 to 20 percent) in these values affect the results of the calculations? If possible, comment on the effect of using the Debye approximation (different crystal vibrational frequencies) for the acoustic lattice modes instead of the Einstein approximation (all the same vibrational frequency). **Not required**

$I_2(s) \dashrightarrow I_2(g).$

$$K_{eq} = \left(\frac{P_{I2(g)}}{X_{I2(s)}} \right)_{eq}$$

If solid is pure $X = 1$

$$\text{where } (P_{I2(g)})_{eq} = [I_2(g)]RT$$

Partial pressure is a very common way of expressing concentration of gases. Does NOT depend on whether other gases are present (if ideal gas behavior)

Iodine is a simple molecule:

We will **NOW** use the **mass, bond length**, **vibrational frequency**, and **heat of sublimation** and **entropy of the crystal** to ***predict*** K_{eq} using **statistical mechanics**

e. Vapor Pressure = K_{eq} = exp(-ΔA^0/RT)

Finally, instead of equation (34), which has been made completely baffling by "simplifying" it to death, we will use $\Delta A = A_{gas} - A_{solid} = -RT\ln Q_{gas} + RTQ_{solid} + \mathbf{\Delta E^0_0(sub)}$ and vary the concentration (which appears in q_{trans} often disguised as the volume,

$V = nRT/p_{I2}$), until we find the pressure that makes **$\Delta A = 0$**. That will be **equilibrium**, and that will be **the "vapor pressure"**

$$\Delta A = A_{vap} - A_{solid}$$

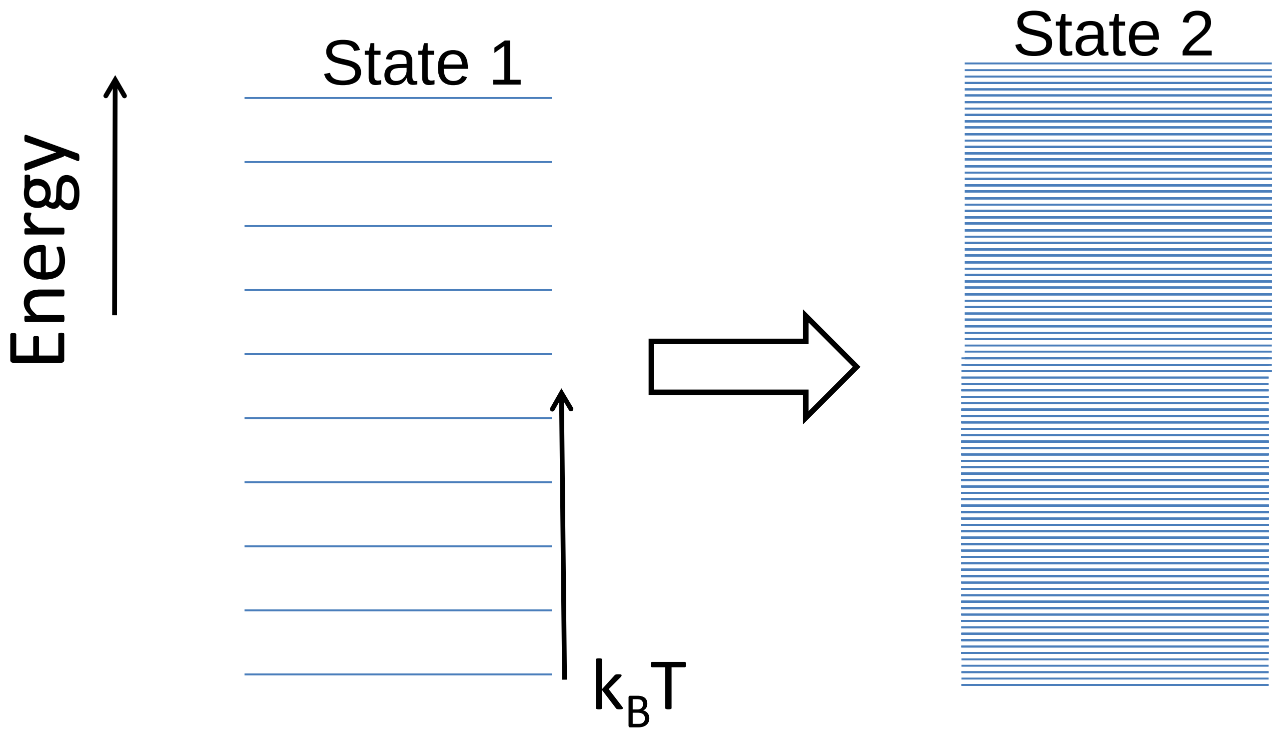
$$\Delta A = -RT\ln\frac{q_{vap}}{q_{solid}} + \Delta E_0^0(sub) = -RT\ln(q_{vap}) + \Delta E_0^0(sub) + RT\ln(q_{solid})$$

$$\Delta A = -RT\ln\left\{[(\tfrac{2\pi mkT}{h^2})^{3/2}\,\tfrac{kT}{p}\times\tfrac{kT}{\sigma hcB_0}\times(1-e^{\frac{-h\nu_{vib}}{kT}})^{-1}]\right\} + \Delta E_0^0(sub) + RT\ln(q_{solid})$$

A Cartoon:

I_2(solid) → I_2(gas)

few vibrational states → very,very,very,...MANY translational states



Equilibrium Constant =

ratio of *available* states

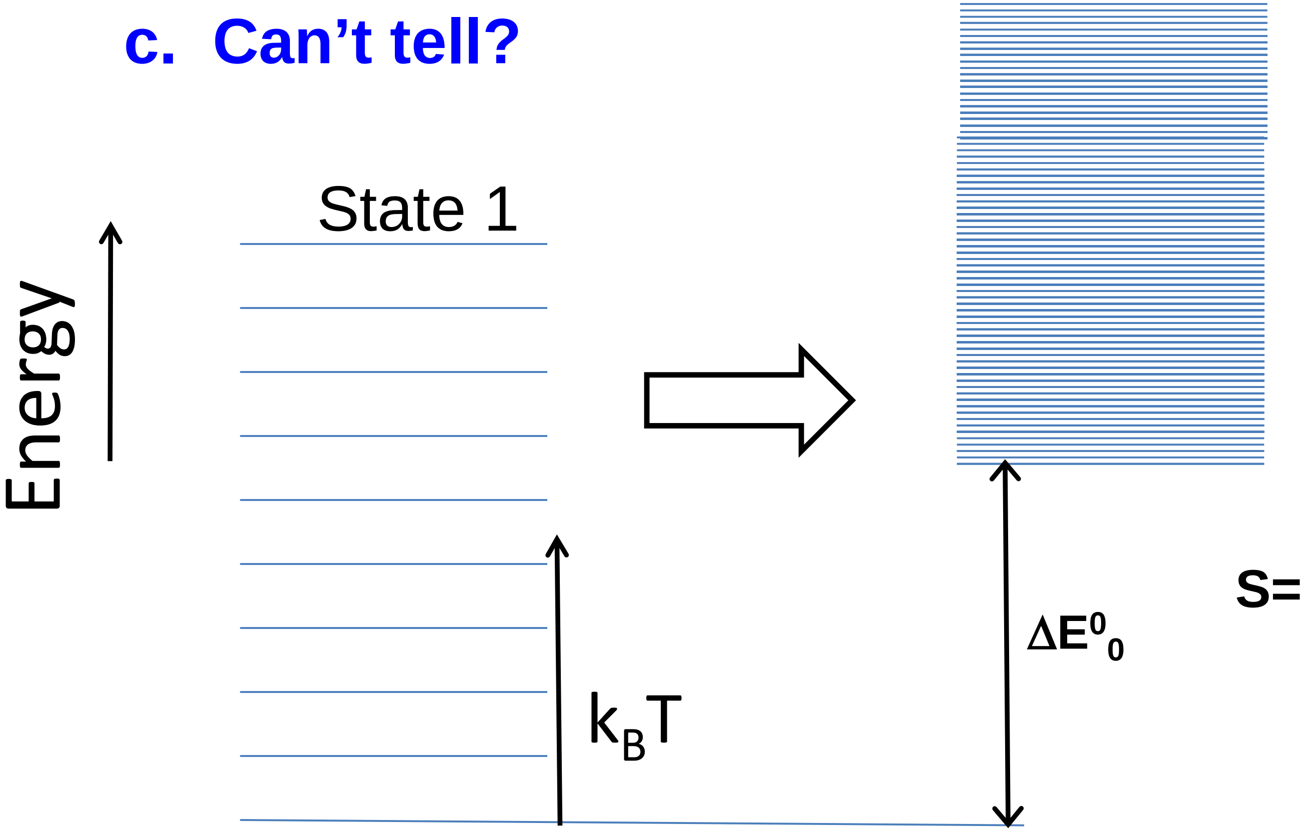
Qualitatively, what will the equilibrium constant, (K =N_2/N_1) be for this system?

3 questions:

a. **Greater than 1 ($\Delta A = \Delta E - T\Delta S$ is negative) ?**

b. **Less than 1 ($\Delta A = \Delta E - T\Delta S$ is positive) ?**

c. **Can’t tell?**



S=R ln (avail. states)

partition function

Partition function = number of ***available*** states

How to get the numbers of states???

Count them

Counting = summing = integration

Will be large if energy level spacing is small

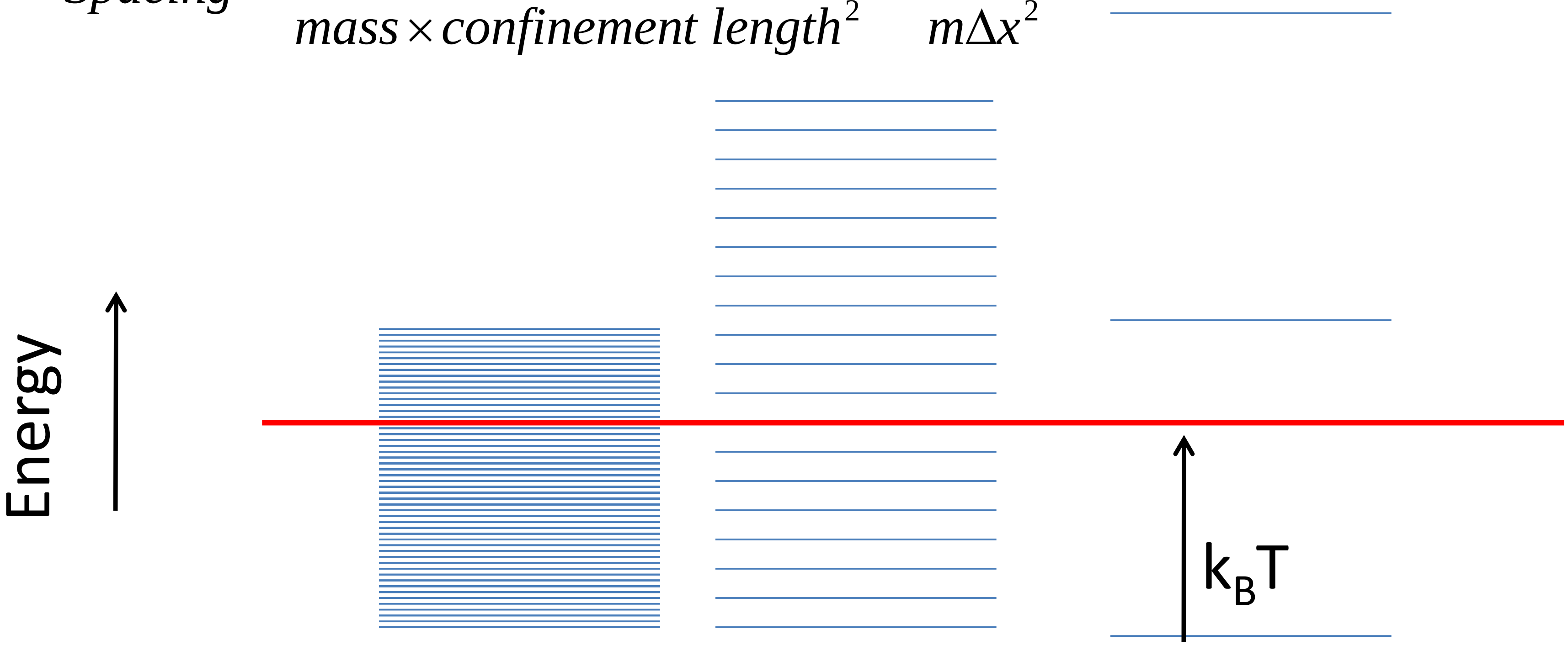
This is **EASILY** determined by quantum mechanics:

What is true of ALL equations for energy levels in quantum mechanics??

$$Spacing \approx \frac{h^2}{mass \times confinement\ length^2} = \frac{h^2}{m\Delta x^2}$$

Effect of energy level spacing on partition function

$$Spacing \approx \frac{h^2}{mass \times confinement\ length^2} = \frac{h^2}{m\Delta x^2}$$



Translational

Δx = **0.01** m

q ~10^{30}

$$q = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V$$

Rotational

Δx = **10^{-10}** m

q ~10^2

$$q = \frac{8\pi^2 I k_B T}{h^2}$$

Vibrational

Δx = **10^{-11}** m

q ~ 2

$$q = \sum_{j=1}^{3N-5} \left(\frac{1}{1 - e^{\frac{-h\nu_{vib}}{kT}}} \right)$$

$$Spacing \approx \frac{h^2}{mass \times confinement\ length^2} = \frac{h^2}{m\Delta x^2}$$

Example: Computing Q for an ideal gas of monoatomic atoms

Quantum mechanics gives the states for a free particle of mass m in a *1-dimensional box* of length a_x

$$\varepsilon_{jx} = \frac{{n_x}^2 h^2}{8m{a_x}^2}, \quad n_x = 1,2,3....$$

Ideal means ***independent*** particles, so that the energy of a system of N atoms will just be the ***sum of the individual energies:***

$$E_{jx} = \sum\nolimits_i \varepsilon_i \, , i = atom\ identifier$$

There is nothing special about x. The energies for the y and z components of kinetic energy are ***independent*** of that for x, so to get the energy and partition functions for the 3 dimensions can be obtained simply from those for 1 dimension.

$E_j = E_{jx} + E_{jy} + E_{jz}$ and $q_{trans} = q_{trans,x}\, q_{trans,y}\, q_{trans,z}$; (the probability of independent events is the product of the individual probabilities.)

Each molecule does its own thing. Therefore the system Q can be written simply from the individual molecule translational partition function:

$$q_{trans,1D} = \sum_j e^{-E_{jx}/k_BT} = \sum_j e^{\frac{-n_{xj}^2 h^2/8ma_x^2}{k_BT}}$$

Because the levels are so closely spaced, the quantum number , $\mathbf{n_{xj}}$ may be considered a continuous variable (atoms behave almost classically) , thus giving

$$q_{trans,1D} = \int_0^\infty e^{\frac{-n_{xj}^2 h^2/8ma_x^2}{k_BT}} dn_x$$

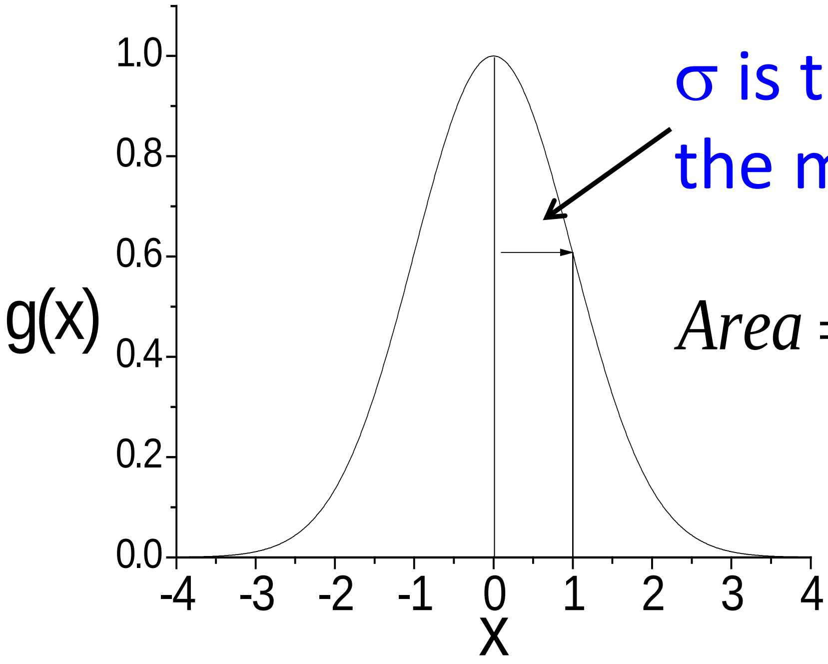
i.e., the integral of is a ***Gaussian*** function, because the variable is squared. We use only half, because n is never negative.

Gaussians

The Gaussian function (“bell-shaped curve”) is so common in science, it is worth spending time getting very familiar with it. Any Gaussian may be written as:

$$e^{\frac{-x^2}{2\sigma^2}}$$

In this form, **σ is the standard deviation,** and of course has the same units as x. This Gaussian has σ = 1.00 and looks like:



σ is the half-width at 0.6065 of the maximum.

$$Area = \int_{-\infty}^{\infty} e^{\frac{-x^2}{2\sigma^2}} dx = (2\pi)^{1/2}\sigma = 2.507$$

In general, the area is always very close to **½ base times altitude**, i.e.,the area of a triangle.

In the integral $q_{trans,x} = \int_0^\infty e^{\frac{-n_x^2 h^2/8ma_x^2}{k_B T}} dn = \text{Area under curve.}$

What is making this integral LARGE? i.e., what makes the exponent small?

Large mass and large space to run around give small energy level spaceing.

Does the Gaussian have large or small standard deviation?

$$\sigma^2 = 4ma^2k_BT/h^2$$

So, $\sigma = (4ma^2k_BT/h^2)^{1/2}$, and the integral under the whole curve is

$(2\pi)^{1/2} (4ma^2k_BT/h^2)^{1/2}$, and half that because the integral starts at 0 gives:

$q_{trans,1D} = (2\pi ma^2k_BT/h^2)^{1/2}$, where a_x is the length of the box.

Because the motion in the 3 dimensions are independent, the 3 D partition function is simply $q_{trans} = (q_{trans,1D})^3 = (2\pi ma^2k_BT/h^2)^{3/2} =$ **$(2\pi mk_BT/h^2)^{3/2}$ V, where $V = a_xa_ya_z$.**

Rotational partition function

$$q_{rotation} = \sum_j e^{-E_{jx}/k_B T} = \sum_j (2J+1) e^{\frac{-J(J+1)h^2/8\pi^2\mu r^2}{k_B T}} \times \frac{h^2/8\pi^2\mu r^2}{k_B T} \times \frac{k_B T}{h^2/8\pi^2\mu r^2}$$

$$\text{but } \frac{\mathrm{dE_J}}{\mathrm{kT}} = \mathrm{d\ J(J+1)} \frac{h^2/8\pi^2\mu r^2}{k_B T} = (2J+1)\frac{h^2/8\pi^2\mu r^2}{k_B T}$$

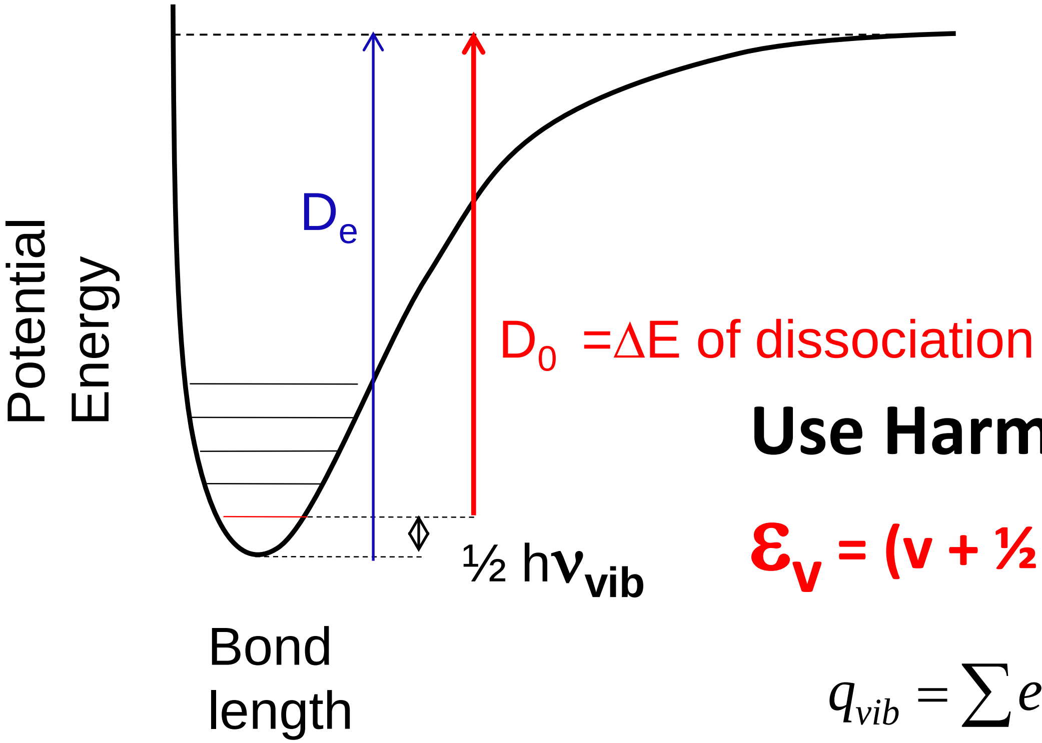
$$q_{rotation} = \frac{-k_B T}{h^2/8\pi^2\mu r^2}\int_0^\infty e^{-x}dx = \frac{-k_B T}{h^2/8\pi^2\mu r^2}[e^{-\infty} - e^{-0}]$$

$$= \frac{k_B T}{h^2/8\pi^2\mu r^2} = \frac{8\pi^2\mu r^2 k_B T}{h^2}$$

Why will this integral be very, very, very much smaller than the translational one?
The mass is same

confinement length = r = the bond length for I_2 = 2.67 Angstroms

Vibrational Partition Function



Use Harmonic Osc. T is not high

$\varepsilon_v = (v + \frac{1}{2})h\nu_{vib}$, with v = 0,1,2,3,

$$q_{vib} = \sum_{v} e^{-(v+\frac{1}{2})\frac{h\nu}{k_B T}} \quad \text{if zero is at bottom}$$

Choosing zero of energy is **arbitrary**
It is ***NEATER*** to choose zero of energy at v=0 instead of bottom of well

$$q_{vib} = \sum_{v} e^{-v\frac{h\nu}{k_B T}} \quad \text{if zero is at } v = 0$$

So, q_{vib} goes to 1 as T goes to 0

Neglecting zero point E gives same number of available states

$\varepsilon_{v} = (v\ )h\nu_{vib}$, with v = 0,1,2,3,

Now energy does not include **zero point vibrational energy**

which does not have anything to do with temperature

$$q_{vib} = \sum_{v} e^{-v\frac{h\nu}{k_B T}} = \sum_{v} e^{-\frac{h\nu}{k_B T}v} == \sum_{v} e^{-\beta h\nu v}$$

$$q_{vib} = \sum_{v} (e^{-\beta h\nu})^{v}$$

$$\text{call} \quad x = e^{-\beta h\nu}$$

$$q_{vib} = \sum_{v} x^{v}, v = 0,1,2,3\ldots$$

$$q_{vib} = (x^{0} + x^{1} + x^{2} + x^{3} + x^{4} + \ldots x^{\infty})$$

$$q_{vib} = (x^0 + x^1 + x^2 + x^3 + x^4 + \ldots x^\infty)$$

$$(x^0 + x^1 + x^2 + x^3 + x^4 + \ldots x^\infty) = \frac{1}{1-x}$$

$$q_{vib} = \frac{1}{1-e^{-\beta h\nu}}$$

$$q_{vib} = \frac{1}{1-e^{\frac{-h\nu}{k_B T}}}$$

Concept of "*vibrational temperature*"

$$q_{vib} = \frac{1}{1 - e^{\frac{-h\nu}{k_B T}}}$$

Obviously, $h\nu/k_B$ has the units of temperature; it is the temperature such that the Boltzmann factor = $\mathbf{e^{-1}}$

A common shorthand is to define $\mathbf{\Theta_{vib} = h\nu/k_B}$

$$q_{vib} = \frac{1}{1 - e^{\frac{-\Theta_{vib}}{T}}}$$

Putting it all together:

For any molecule:

$q = q_{trans} q_{rot} q_{vib} q_{elec}$

For a linear polyatomic molecule:

$$q = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \cdot \frac{T}{\sigma \Theta_{rot}} \cdot \sum_{j=1}^{3N-5} \left(\frac{1}{1-e^{\frac{-\Theta_{vib}}{T}}}\right) \cdot \sum_i g_{elec,i} e^{\frac{-E_{elec,i}}{k_B T}}$$

What is **σ** ??? This is NOT standard deviation; it is the "SYMMETRY NUMBER"

For a ***homonuclear*** diatomic **σ = 2**, because the total wavefunction must either be symmetric or anti-symmetric to interchange of two identical particles. Recall that exchange of identical electrons requires the wavefunction to change sign. This leads to the Pauli exclusion principle for all fermions, e.g., electrons.

Iodine is a fermion because it has 53 protons and 74 neutrons, an odd number of fermions. Because the rotational functions with even J are symmetric, **they will not be occupied.** A good approximation is to divide by 2 because ***roughly*** **half** of the rotational states cannot be occupied.

e. Vapor Pressure = K_{eq} = exp(-ΔA^0/RT)

Finally, instead of equation (34), which has been made completely baffling by "simplifying" it to death, we will use $\Delta A = A_{gas} - A_{solid} = -RT\ln Q_{gas} + RTQ_{solid} + \mathbf{\Delta E^0_0(sub)}$ and vary the concentration (which appears in q_{trans} often disguised as the volume,

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