HEAT CAPACITY (C_p/C_v)

NOTATION NOTES:

1. S,G,&N uses E for internal energy (vs. U as given in most P-Chem textbooks);
2. Molar quantities (e.g. C_p/n) : C_p , C_v etc. are indicated with a "squiggle" on top. These are also indicated as $C_{p,m}$ in the notes.

Heat capacity is the ability of a particular substance (atom or molecule) to "absorb" energy when its temperature is raised.

The energy that is absorbed must take the form of internal energy of the absorber (e.g. motion).

Energy : Capacity to do work

Classical (Newtonian): $KE = \frac{1}{2}mv^2$

Define the <u>Degrees of Freedom</u> as the number of ways a molecule can move:

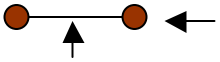
Need 3N (N = number of atoms) coordinates/atom to specify the unique position in space of a molecule

- **Translational** (Center of mass moving through space)

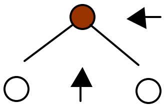
3 translational “modes” (x, y, and z) … velocity and kinetic energy component is associated with each dimension. Since there are three per atom, there are 3N translational degrees of freedom/molecule.

- **Rotational** (rotation about the center of mass)

Linear: 2 unique rotations



Non-linear: 3 unique rotations



And one axis perpendicular to page

- What is left is **vibrational**:

$3N - 5$ for linear ($5 = 3$ for translational + 2 for rotational)

$3N - 6$ for non-linear ($6 = 3$ for translational + 3 for rotational)

How much energy is associated with each degree of freedom? Must depend on T.

Equipartition theorem

(1) Qualitative: The energy levels associated with the different motions are equally populated. Thus, each degrees of freedom has the save average energy:

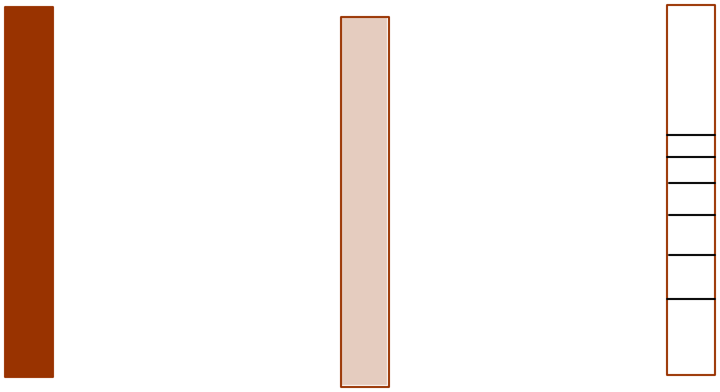
e.g. an x-translation, y-translation, z-translation each has the same energy as each rotational and vibrational mode

(energy is equally partitioned over all available modes)

(2) Quantitative: The average energy associated with each degree of freedom is ½kT or (on a molar basis) ½RT ($R = N_A k$)

Problem: Equipartition theorem is derived from classical physics, which "allows" any value of the energy. Attempts to use the laws of classical physics to derive rotational and vibrational energies failed (theory could not explain what was experimentally observed). Thus the advent of Quantum Mechanics, where the state is defined by a unique set of quantum numbers (c.f. Chem 302).

The equipartition theorem is not valid if energy levels are quantized:



Translational:
"continuum" of states

Rotational:
"quantized" states
(separation of ca. 1 cm^{-1})

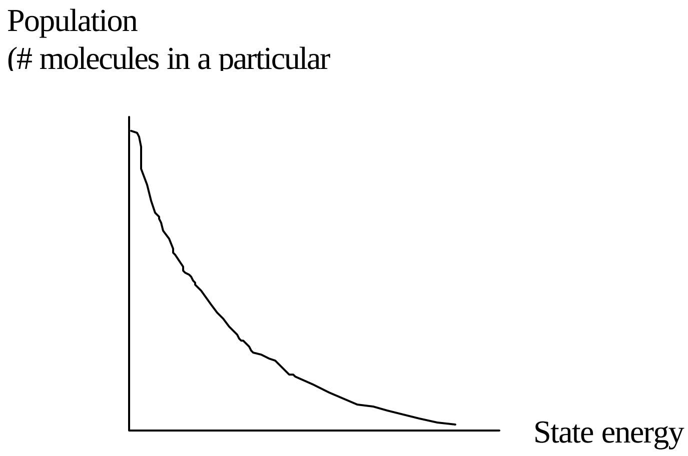
Vibrational:
"quantized" states
(separation of ca. 100 - 3000 cm^{-1})

(a) OK for translations, since this motion is classical

(b) In a strict sense, it does not apply to rotations, since these levels are quantized. However, since the energy spacing is small and many states are populated, it turns out to be o.k. at room temp.

Consider the state populations as distributed by Boltzmann:

Boltzmann: $N_i/N_j = \exp[-(E_i-E_j)/kT]$



From the above eq., rotational population differences are calculated:

$$\frac{\Delta E}{kT} = \frac{1\text{cm}^{-1}(\frac{\text{cm}}{\text{s}})(\text{J}-\text{s})}{\frac{\text{J}}{\text{K}}(\text{K})} = \frac{1(3\text{e}10)(6.626\text{e}-34)}{(1.38\text{e}-23)(298)} \approx 0.005$$

therefore, not much difference in population: N_i/N_j ca. 1

(c) Not o.k. for vibrational motion. Why?

Vibrational population differences: $\frac{\Delta E}{kT} = 4.8$ or $N_i/N_j = 0.01$ (100 times more molecules in the lower level)

Relationship to Heat Capacities:

(1) For a perfect monoatomic gas (3 translational modes only)

$$C_{v,m} = \left(\frac{\partial U}{\partial T}\right)_v = 3/2\ R$$

(2) Diatomics and polyatomics: must add rotational and vibrational contributions (Total internal energy = sum of the three).

$C_{v,m} = 3/2\ R + 2(1/2R) + (3N - 5)(1/2R)$ for a linear molecule

For non-linear molecules, there are 3 rotational degrees of freedom and rotational contribution is 3(1/2R).

For non-linear polyatomics, the translational (3 d.f.'s) and rotational contributions (3 d.f.'s) to heat capacity gives:

$$C_{v,m} = 3\ R$$

What about vibrational contributions?

Quantum mechanics gives the expression for vibrational energy in each mode. Differentiation with respect to T yields the expression for the vibrational contribution to heat capacity:

$$C_{v,m} = R\ f^2$$

Where $f^2 = \left(\frac{h\upsilon}{kT}\right)^2 \left(\frac{e^{-\frac{h\upsilon}{kT}}}{(1-e^{-\frac{h\upsilon}{kT}})^2}\right)$

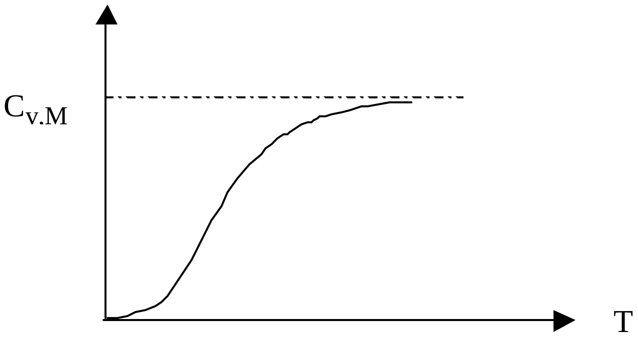
Expanding in a Taylor series: $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots$

$$f^2 = \left(\frac{h\upsilon}{kT}\right)^2 \left[\frac{1 - \frac{h\upsilon}{kT} + \ldots}{1 - \left(1 - \left(\frac{h\upsilon}{kT}\right) + \ldots\right)^2}\right] \text{ca. 1 at high T}$$

**** At high T, the equipartition theorem predicts that the vibrational contribution to $C_{v,M}$ FOR EACH MODE is given by R.

**** At low T, $C_{v,M} < R$

(Question to ponder in your lab report: Is the vibrational contribution significant for N_2 and CO_2? How does the contribution compare to that predicted by the equipartition theorem?



Relationship between C_p and C_v:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p ; \; C_v = \left(\frac{\partial U}{\partial T}\right)_v ; \; H = U + PV$$

Using the above relationships, can write:

$$C_p = \left[\frac{\partial(U+PV)}{\partial T}\right]_p = \left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P = C_V + (P)(\frac{nR}{P})$$

Thus: $C_p = C_v + R$

Dividing through by C_v:

$\frac{C_p}{C_v} = 1 + \frac{R}{C_v}$ The theoretical heat capacity ratio

DO: Compare a measured heat capacity ratio with that predicted by equipartition.

To do so, you need to calculate C_v for each of the three molecules … diatomic and triatomic need to add rotational and vibrational

Conclusion: When the equipartion theorem is valid:

(1) Translational energy is given by 3N (1/2RT) and C_v = 3/2R.

(2) Rotational energy is given by 2 (1/2RT) for a linear molecule or 3 (1/2RT) for a non-linear molecule.

(3) Vibrational energy, IF T IS LARGE, is given by: (# modes) RT. If T is small, then the vibrational component deviates from this maximum value.