CHAPTER 11 –Energy Levels

In Chapter 10 we learned about energy distributions and ensembles. In chapter 11 we build on those ideas by using simple models for a gas molecule's (or atom's) ladder of energy levels.

Salient points from Chapter 10

1) Eqn 10.2: $U = <E> = \sum_j p_j E_j$ where $p_j = \dfrac{exp(-\frac{E_j}{kT})}{\sum_j exp(-\frac{E_j}{kT})}$ Eqn 10.9

2) Eqn 10.10: $Q = \sum_j exp\left(-\frac{E_j}{kT}\right)$

For independent subsystems (i.e., gas atoms or molecules),
$Q=q^N$ if distinguishable (Eqn10.28); and $Q=q^N/N!$ if distinguishable (Eqn 10.30)

3) We can calculate thermodynamic functions and properties from the partition function

Eqn 10.35: $<E> = U = kT^2 \left[\frac{\partial lnQ}{\partial T}\right]$

Eqn 10.39: $S = k\, lnQ + \frac{U}{T}$

Can use thermodynamic definitions (such as F=U-TS) and relationships (such as $p = -\left(\frac{\partial F}{\partial V}\right)$) to find the rest; see Table 10.1 for some examples

Translational Energy Levels

Use Particle-in-box Model
(1-dimensional)

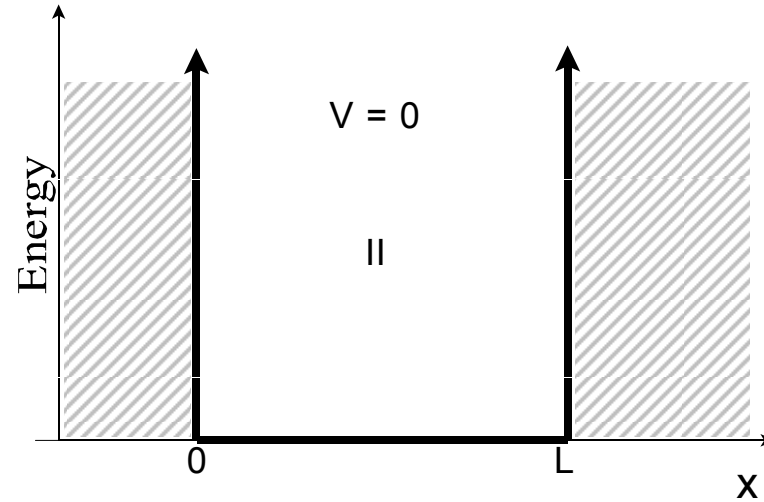$$\varepsilon_n = \frac{n^2 h^2}{8mL^2}$$

$$q_{tr} = \sum_{n=1}^{\infty} e^{-n^2 h^2 / 8mL^2 kT} = \sum e^{-n^2 \theta_{tr}/T}$$

- -

For Ar in 1 cm box

$$\theta_{tr} = \frac{h^2}{8mL^2} = 6 \times 10^{-16} K$$

- -

if $\theta/T << 1$

$$q_{tr} \approx \int_0^{\infty} e^{-n^2 \theta_{tr}/T} dn \quad \Bigg| \quad \int_0^{\infty} e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

A potential energy diagram for the one-dimensional particle in a box is drawn here.

$$q_{tr} = \left(\frac{2\pi mkT}{h^2} \right)^{1/2} L$$

What about a 3D box?

For 3D box of sides of length *a, b,* and *c,* the energy can be written as

$$\varepsilon_{n_x,n_y,n_z} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

So that q_{tr} is a product of three one dimensional translational partition functions

$$q_{tr} = q_x q_y q_z = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} abc = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V = \frac{V}{\Lambda^3}$$

For Argon T = 273 K, V = 224 x 10^{-2} m^3 for 1 mole, p = 1 atm

$$q_{tr} = 2.14x10^{32}V = 4.79x10^{39} \quad \text{states/atom}$$

Even for the lightest molecules, H_2, this approximation is good at room temperature

$$\Lambda = 0.714 \text{ Å for } H_2 @T = 300 \text{ K} \quad \text{so that} \quad q_{tr} = 2.7 \text{ x } 10^{24} \text{ states per molecule}$$

What is the average energy of a monatomic ideal gas atom?

Use the translational partition function to prove that the average energy of an ideal monatomic gas atom given by 1.5 k T.

Use $\quad <\varepsilon_{tr}> = kT^2 \left(\frac{\partial ln q_{tr}}{\partial T}\right)$ Eqn 10.36 $\quad$ and $\quad q_{tr} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$

$$<\varepsilon> = kT^2 \left(\frac{\partial ln q_{tr}}{\partial T}\right)$$

$$= kT^2 \left[\frac{\frac{\partial q_{tr}}{\partial T}}{q_{tr}}\right] = kT^2 \left[\frac{\left(\frac{2\pi mk}{h^2}\right)^{3/2} V}{\left(\frac{2\pi mk}{h^2}\right)^{3/2} V} \frac{\frac{\partial}{\partial T} T^{3/2}}{T^{3/2}}\right]$$

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

What about ideal gas molecules ?

A potential energy surface is sketched for the ground electronic state of a diatomic molecule.

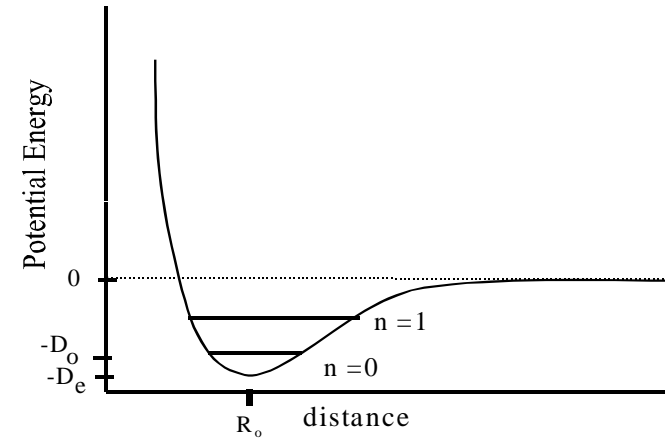Assume separability for different degrees of freedom

$$\varepsilon_j = \varepsilon_{j,trans} + \varepsilon_{j,rot} + \varepsilon_{j,vib} + \varepsilon_{j,elec}$$

For their partition functions we find

$$q = \sum_{j=1}^{M} g_i \exp\left(-\beta\left(\varepsilon_{j,trans} + \varepsilon_{j,rot} + \varepsilon_{j,vib} + \varepsilon_{j,elec}\right)\right) = q_{trans}\, q_{rot}\, q_{vib}\, q_{elec}$$

The average energies become

$$<\varepsilon> = <\varepsilon_{trans}> + <\varepsilon_{rot}> + <\varepsilon_{vib}> + <\varepsilon_{elec}>$$
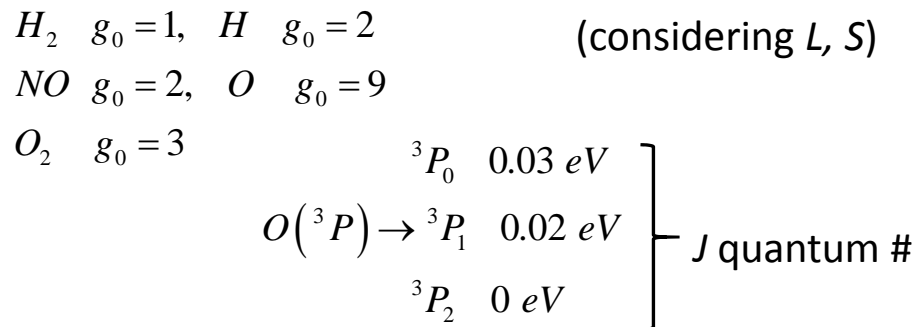
Can we find q_{elec}?

Each molecule (or atom) has its own unique ladder of electronic energy states. Thus, we have no simple model and we must evaluate the electronic partition function sum explicitly.

$$q_{el} = \sum_{i=1} g_i \, e^{-\varepsilon_i/kT}$$

$$q_l = g_0 + g_1 e^{-\Delta\varepsilon_1/kT} + g_2 e^{-\Delta\varepsilon_2/kT} + \ldots$$

degeneracies

$H_2 \quad g_0 = 1, \quad H \quad g_0 = 2$ (considering *L, S*)

$NO \quad g_0 = 2, \quad O \quad g_0 = 9$

$O_2 \quad g_0 = 3$

$$O\left({}^3P\right) \rightarrow \left.\begin{array}{l} {}^3P_0 \quad 0.03 \; eV \\ {}^3P_1 \quad 0.02 \; eV \\ {}^3P_2 \quad 0 \; eV \end{array}\right\} \; J \text{ quantum \#}$$
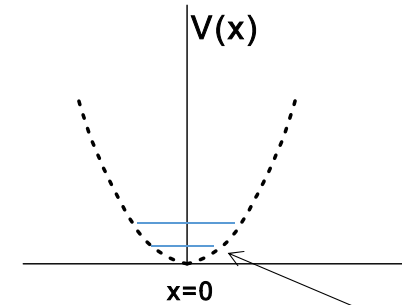
Fortunately, most electronic states are separated from the ground state by a large energy gap, so that we only need to evaluate the first term, or the first few terms in the partition function summation.

For q_{vib} we can find a closed for expression in the harmonic oscillator approximation

Vibration model

$$\varepsilon_V = \left(v + \frac{1}{2}\right)h\upsilon, \quad v = 0, 1, 2, \ldots$$

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}, \quad \text{where } k = \text{force constant}$$

V(x)

x=0

Start zero from ground vibrational level.

$$q_{vib} = \sum_{0}^{\infty} e^{-v h\upsilon/kT} = 1 + x + x^2 \ldots, \quad x = e^{-h\upsilon/kT} \qquad \text{where } k = \text{Boltzmann constant}$$

$$q_{vib} = \frac{1}{1-x} = \frac{1}{1 - e^{-h\upsilon/kT}}$$

O_2: T = 298 K, q_{vib} = 1.0005
 T = 1000 K, q_{vib} = 1.11

Finding the average vibrational energy of a diatomic

The average energy is given by

$$<\varepsilon_{vib}> = kT^2 \left(\frac{\partial \ln q_{vib}}{\partial T}\right) \text{ and } \qquad q_{vib} = \frac{1}{1-x} = \frac{1}{1-e^{-h\upsilon/kT}}$$

$$<\varepsilon_{vib}> = \frac{\theta_{vib} \, k \, e^{-\theta_{vib}/T}}{\left(1 - \exp(-\theta_{vib}/T)\right)} = \frac{h\nu \, e^{-\theta_{vib}/T}}{\left(1 - \exp(-\theta_{vib}/T)\right)} \qquad \text{where } \theta_{vib} = h\nu/k$$

$$O_2: \qquad \theta_{vib} = 2256 \text{ K}$$
$$T = \ 298 \text{ K}, <\varepsilon_{vib}> = 0.814 \text{ cm}^{-1}$$
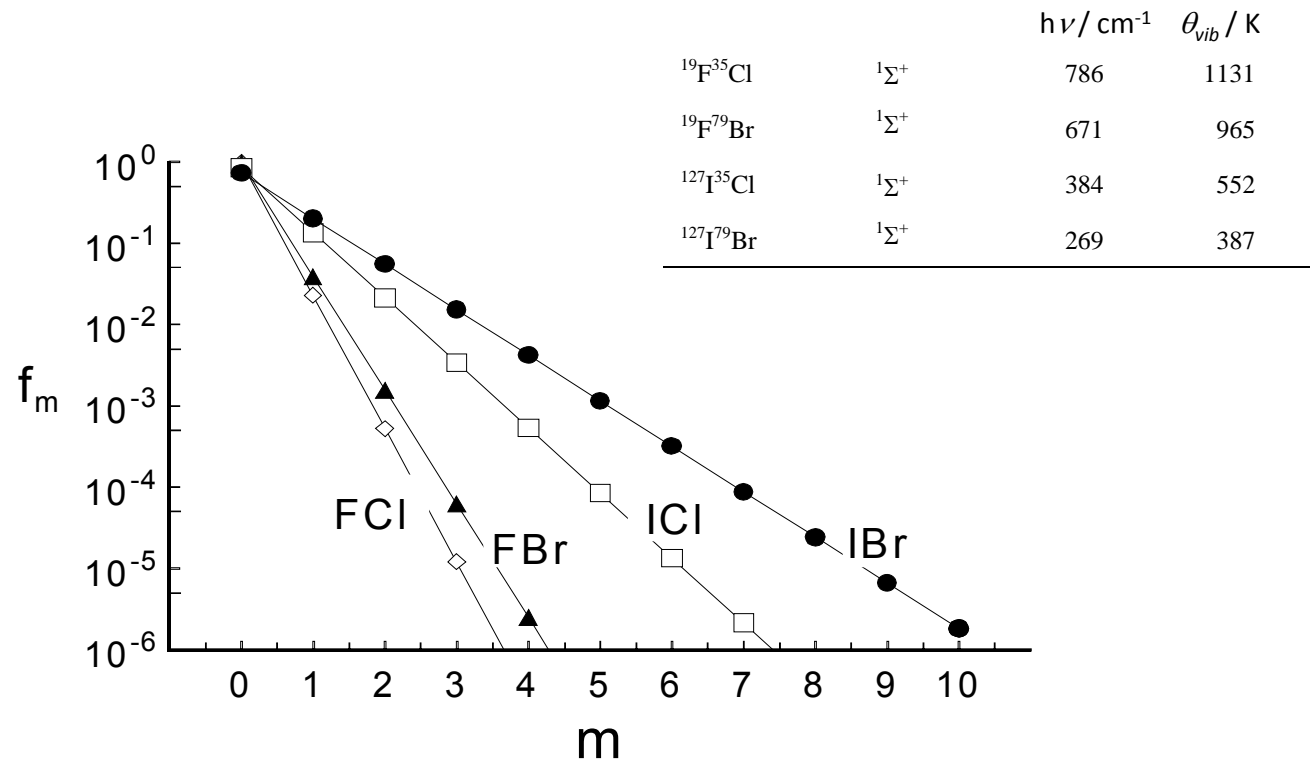$$T = 1000 \text{ K}, <\varepsilon_{vib}> = 183 \ \text{ cm}^{-1}$$

In the high temperature limit, we find that $q_{vib} \rightarrow kT/h\nu$ and $<\varepsilon_{vib}> = kT$.

For polyatomics

$$\varepsilon_{vib} = \sum_{i=1}^{3n-6(5)} \varepsilon_i \quad \text{and} \quad q_{vib} = \prod_{i=1}^{3n-6(5)} \left(\frac{1}{1 - \exp(-\theta_i/T)}\right) \qquad <\varepsilon_{vib}> = \sum_{i=1}^{3n-6(5)} \left(\frac{h\nu_i}{\left(\exp(\theta_i/T) - 1\right)}\right)$$

Populations in vibrational energy levels of diatomics

$$P_m = f_m = \exp(-m\,\theta_{vib}/T)(1-\exp(-\theta_{vib}/T))$$

		$h\nu$ / cm^{-1}	θ_{vib} / K
$^{19}F^{35}Cl$	$^1\Sigma^+$	786	1131
$^{19}F^{79}Br$	$^1\Sigma^+$	671	965
$^{127}I^{35}Cl$	$^1\Sigma^+$	384	552
$^{127}I^{79}Br$	$^1\Sigma^+$	269	387

This figure shows the fractional population of vibrational levels for FCl (○), FBr (▲), ICl (□), and IBr (●).

Can we find q_{rot} for rotational energy levels ?

Rigid rotor model: $\varepsilon_\ell = \dfrac{\ell(\ell+1)h^2}{8\pi^2 I}$ $\qquad$ $\theta_{rot} = \dfrac{h^2}{8\pi^2 I k}$

$\ell = $ angular momentum quantum #
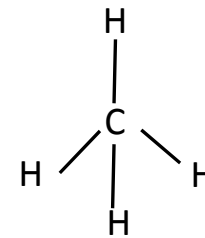
$I = $ moment of inertia

$$q_{rot} = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\varepsilon_\ell / kT}$$

for $T \gg \theta_{rot}$

$$q_{rot} = \int_0^\infty (2\ell+1) e^{-\varepsilon_\ell / kT} d\ell = \frac{T}{\sigma \theta_{rot}} = \frac{8\pi^2 I k T}{\sigma h^2}$$

$$O_2, \quad 298K, \quad q_{rot} = 72$$

$\sigma = $ symmetry factor (accounts for overcounting of states)

$A-B \quad \sigma = 1$

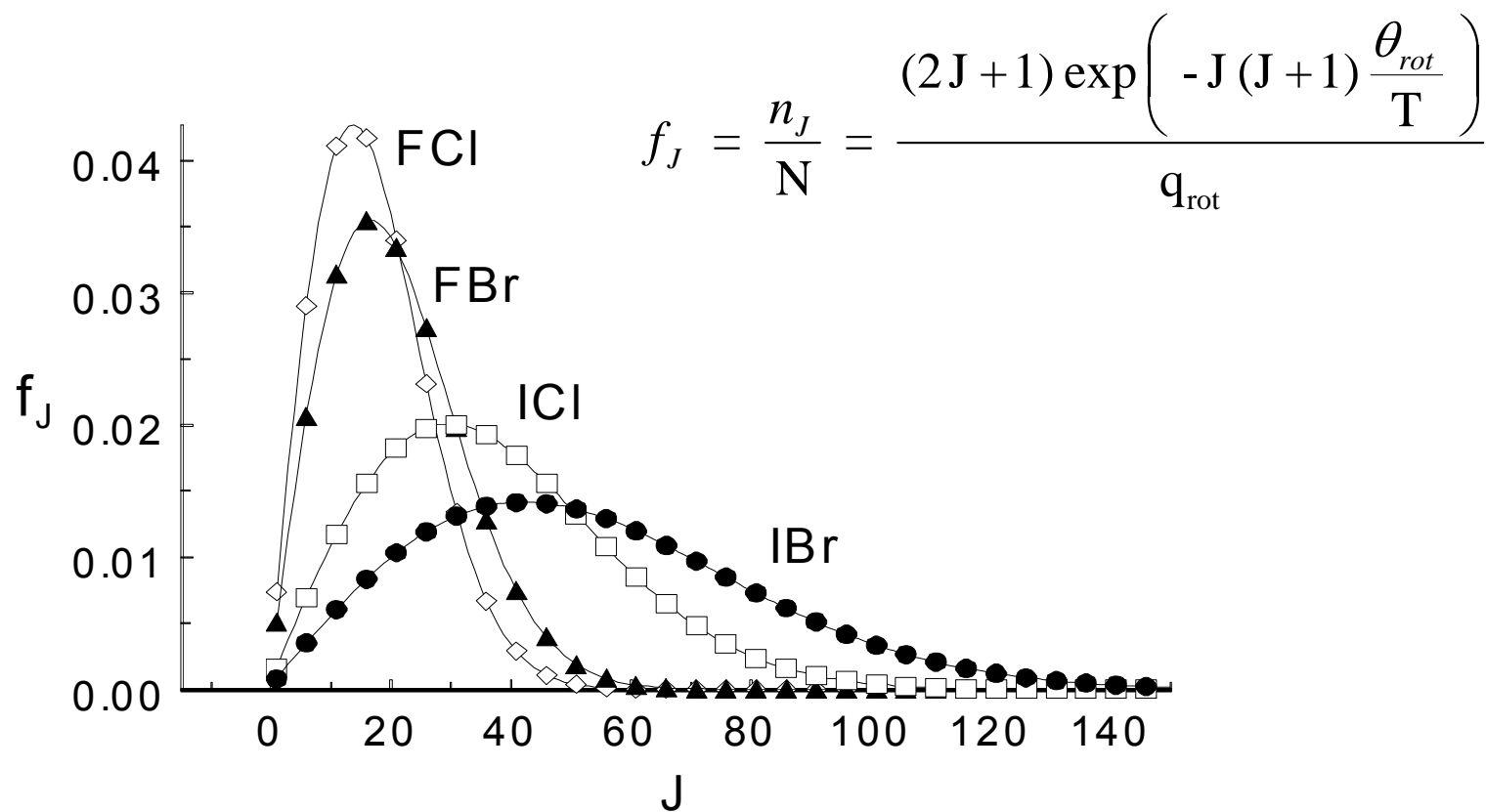$A-A \quad \sigma = 2$

$H_2O \quad \sigma = 2$

$CH_4 \quad \sigma = 12$

$C_6H_6 \quad \sigma = 12$

For nonlinear molecules

$$q_{rot} = \frac{\sqrt{\pi I_a I_b I_c}}{\sigma} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2}$$

Populations in rotational energy levels of diatomics

$$f_J = \frac{n_J}{N} = \frac{(2J+1)\exp\left(-J(J+1)\dfrac{\theta_{rot}}{T}\right)}{q_{rot}}$$

The population distribution of rotational energy levels is shown here for four interhalogen molecules.

Let's put the pieces together and build the total partition function

$$q = q_{tr}q_{rot}q_{vib}q_{el}$$

Consider a linear diatomic with $q_{el} = 1$

$$q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \left(\frac{8\pi^2 IkT}{\sigma h^2}\right)\left(\frac{1}{1-e^{-h\upsilon/kT}}\right)$$

Ideal gas (indistinguishable particles)

$$F = -kT\ell nQ = -kT\ell n\left(\frac{q^N}{N!}\right) = -NkT\ell n\left(\frac{eq}{N}\right)$$

using Stirling's approximation

$$\ell n\left[\frac{q^N}{N!}\right]$$
$$= N\ell nq - N\ell nN + N$$
$$= N\ell nq - N\ell n(N) + N\ell n(e)$$
$$= N\ell n\left(\frac{eq}{N}\right)$$

$$F = -NkT\left[\ell ne + \ell nq - \ell nN\right], \quad q = q_iV$$
$$F = -NkT\left[\ell ne + \ell nq_0 + \ell nV - \ell nN\right]$$

Now we can find thermodynamic relations

1) Use $F = -NkT\left[\ell ne + \ell nq_0 + \ell nV - \ell nN\right]$ to find the ideal gas equation of state

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = +\frac{NkT}{V} \qquad \text{or} \qquad pV = NkT$$

2) Use $U = NkT^2 \dfrac{\partial \ell nq}{\partial T}$ to find the internal energy

$$U = <E> = \sum_{i=1}^{N} <\varepsilon_{total}> = \frac{3}{2}NkT + \sum_{n=1}^{3(2)} \frac{1}{2}NkT + \sum_{i=1}^{3n-6(5)} \left(\frac{Nh\nu_i}{e^{\theta_i/T} - 1}\right) - ND_0$$

3) For the constant volume heat capacity we find

$$C_V = \left(\frac{\partial <E>}{\partial T}\right)_V = \frac{3}{2}Nk + \sum_{n=1}^{3(2)} \frac{1}{2}Nk + \sum_{i=1}^{3n-6(5)} (Nk)$$

In Class Problem

A. The heat capacities of Ne and Xe are the same at T = 300 K! What is the value of their constant volume heat capacity? Why are their heat capacities the same?

B. The heat capacity of a diatomic gas is always higher than that of a monatomic gas, if the total mass is the same and if the conditions are similar. Why is the heat capacity of a diatomic gas higher and what range of values may it take?

C. The heat capacity of molecules is temperature dependent, even for an ideal gas of molecules. Explain why this is so!

The constant pressure heat capacity

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = C_V + R$$
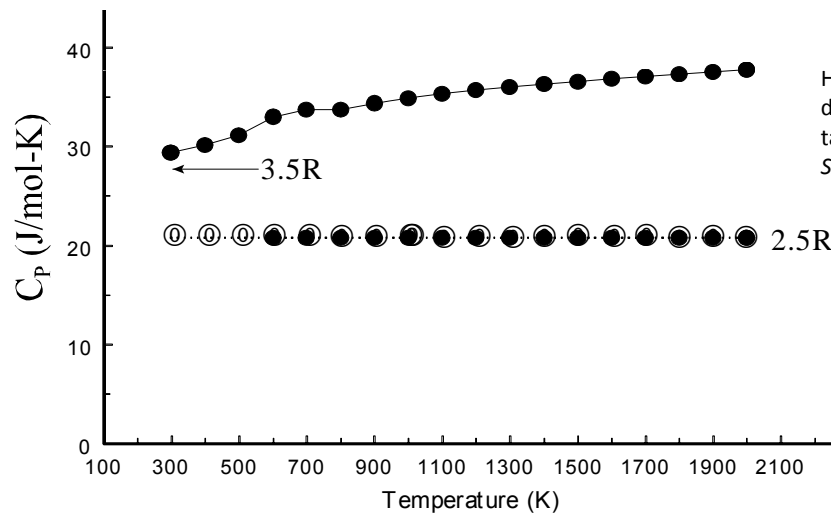
Heat capacity data for monatomic gases and diatomic oxygen are shown here. The data were taken from I. Barin, *Thermochemical Data of Pure Substances.*

We can calculate the Entropy

$$<S> \ = \ k \ ln\!\left(\frac{q^N}{N!} \right) + \frac{<E>}{T} \ = \ k \ lnQ + \frac{<E>}{T} \ = \ k \ lnQ + k \ T\!\left(\frac{\partial \, lnQ}{\partial \, T} \right)_{\!V}$$

Use $\ q \ = \ \left(\dfrac{2 \, \pi \, m \, k \, T}{h^2} \right)^{3/2} V \quad ; \quad <E> \ = \ \dfrac{3}{2} \, Nk \, T$

to show that $\quad <S> \ = \ Nk \ ln\!\left(\dfrac{(2 \, \pi \, m \, k \, T)^{3/2} \, V \, e}{N \, h^3} \right) + \dfrac{3}{2} \, Nk$

or

$$<S> \ = \ \frac{5}{2} \, Nk + Nk \ ln\!\left(\left(\frac{2 \, \pi \, m \, k \, T}{h^2} \right)^{3/2} \frac{V}{N} \right) \ = \ \frac{3}{2} \, Nk \ lnM + \frac{3}{2} \, Nk \ lnT + Nk \ lnV + K'$$

In Class Problem

Consider the absolute entropies for the gases shown on the right. Explain the trend in the entropies for the monatomic series of gases.

He	126.0
Ne	146.2
Ar	154.7
Kr	164.0
Xe	170.0
Hg	175.0

We can calculate the chemical potential of an ideal gas

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -\frac{\partial}{\partial N}\left[NkT\ell n\left(\frac{eq}{N}\right)\right]_{T,V} = -kT\ell n\left(\frac{eq}{N}\right) + NkT\frac{1}{N}$$

$$= kT\ell n\left(\frac{N}{eq}\right) + kT = -kT\ell n\left(\frac{q}{N}\right)$$

If we write $\quad q = q_0 V = \dfrac{q_0 NkT}{p}$

then we find that $\quad \mu = -kT\ell n\left(\dfrac{q_0 kT}{p}\right) = kT\ell n\dfrac{p}{p_{\text{int}}^0} \qquad$ with $\quad p_{\text{int}}^0 = q_0 kT$

$p_{\text{int}}^0 = $ standard state pressure

In an alternative form, we find

$$\mu_0 = -kT\ell n p_{\text{int}}^0 \Rightarrow \mu = \mu^0 + kT\ell n p \qquad\qquad \mu^0 = \text{ standard state chemical potential}$$

Equipartition theorem

$$\langle \varepsilon \rangle = \frac{\sum\limits_{x} \varepsilon(x) e^{-\varepsilon(x)/kT}}{\sum\limits_{x} e^{-\varepsilon(x)/kT}}, \quad x \text{ a degree of freedom}$$

$$\langle \varepsilon \rangle = \frac{\int_{-\infty}^{\infty} \varepsilon(x) e^{-\varepsilon(x)/kT} dx}{\int_{-\infty}^{\infty} e^{-\varepsilon(x)/kT} dx}$$

Suppose $\varepsilon(x) = cx^2$

$$\langle \varepsilon \rangle = \frac{1}{2} kT$$

$$\langle x^2 \rangle = \frac{kT}{2c} : \text{fluctuations}$$

$$\langle \varepsilon^{vib} \rangle = kT \qquad \text{(both KE, PE)}$$

$\varepsilon_n^{trans} \qquad \alpha n^2$

$\varepsilon_e^{rot} \qquad \alpha \ell(\ell+1)$

$\varepsilon_v^{vib} \qquad \alpha = \left(v + \frac{1}{2} \right) h\nu$

only holds at very high T

Einstein model of solids

N atoms $\Rightarrow \dfrac{C_v = 3Nk}{Dulong + Petit}$ $\Big|$ equipartition

actual at low $T, C_v \to 0$ (as explained by Einstein)

Einstein: solid = *3N* oscillators

$$q = \left(1 - e^{-\beta h\nu}\right)^{-1} \to \langle\varepsilon\rangle = h\nu\left(\dfrac{e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}\right)$$

$$C_v = 3N\dfrac{\partial\langle\varepsilon\rangle}{\partial T} = 3Nk\left(\dfrac{h\nu}{kT}\right)^2\dfrac{e^{-h\nu/kT}}{\left(1 - e^{-h\nu/kT}\right)^2} \quad\nearrow\quad 0 \text{ as } T \to 0$$

$$\searrow 3Nk\left(\dfrac{h\nu}{kT}\right)\left(\dfrac{1 - h\nu/kT}{1 - 1 + \left(h\nu/kT\right)^2}\right) = 3Nk \text{ as } T \to 0$$

actually $C_v \sim T^3$ at low *T*

        (explained by Debye model)