



XVTH INTERNATIONAL CONFERENCE  
ON RAMAN SPECTROSCOPY

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AUGUST 11-16, 1996  
PITTSBURGH, PA, U.S.A.

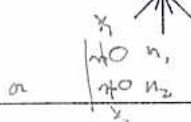
Organizing Committee:  
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R. D. Coalson  
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(noninteracting)  
Composite system:



$$E = E_A^j + E_B^k$$

separation of internal motions:



← identical distinguishable subsystems.

Assuming distinguishable A, B:

$$Q = \sum_i \sum_k e^{-\beta(E_A^i + E_B^k)} = \left( \sum_i e^{-\beta E_A^i} \right) \left( \sum_k e^{-\beta E_B^k} \right) = Q_A Q_B$$

NB: for indistinguishable A, B:

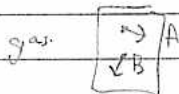
$$Q \approx \frac{q^N}{N!}$$

(generic)

[g = molecular p.f.]

← Boltzmann statistic

(applies for molecules, except at very low T)



N indistinguishable particles

So for a gas of molecules (noninteracting)

$$Q \approx \left( \text{partition function for one molecule} \right)^N / N!$$

Atkins def.

NB: to connect Q to Atkins, note

$$Q = e^{-\beta E_0} \sum_i e^{-\beta(E_i - E_0)}$$

↑  
ground state energy

then:

$$\ln Q = -\beta E_0 + \ln \sum_i e^{-\beta(E_i - E_0)} \quad A = -k_B T \ln Q = -k_B T \left[ -\beta E_0 + \ln \sum_i e^{-\beta(E_i - E_0)} \right]$$

$$= E_0 - k_B T \ln Q$$

thus:

$$A - E_0 = -k_B T \ln Q$$

A(0)

$$A(0) = -k_B T \ln \sum_i e^{-\beta E_i} = E_0$$


↑  
T=0


So, Atkins' version is

$$A - A(0) = -k_B T \ln Q \quad (\text{eq. Table 20.1}) \quad (\text{similarly for } S, U)$$

↑ measuring from E<sub>0</sub>.

Background Facts for Sackur-Tetrode calculation

① Translational p.f.  in 1D,  $g \approx a \left( \frac{2\pi m}{h^2} \right)^{1/2}$ ,  $\lambda = \left( \frac{h^2}{2\pi m k_B T} \right)^{1/2}$  = thermal de Broglie wavelength

then in 3D:   $g = \left( \frac{a}{\lambda} \right)^3 = \frac{V}{\lambda^3}$ ,  $V$  = container volume

translational  
Internal energy of a monoatomic gas particle (atom) in 3D:

$$\langle E \rangle = \frac{\int \frac{1}{2} p^2 g}{g} = \frac{\int \frac{1}{2} \left( \frac{1}{\lambda^3} \right)}{\left( \frac{1}{\lambda^3} \right)} = \frac{\int \frac{1}{2} \left( \frac{1}{\beta} \right)^{3/2}}{\left( \frac{1}{\beta} \right)^{3/2}} = \frac{1/2}{1} \frac{\left( \frac{1}{\beta} \right)^{3/2}}{\left( \frac{1}{\beta} \right)^{3/2}} = \frac{3}{2} \frac{1}{\beta} = \frac{3}{2} k_B T$$

cf. classical equipartition thm: (Atkins, Sect. 2.2)

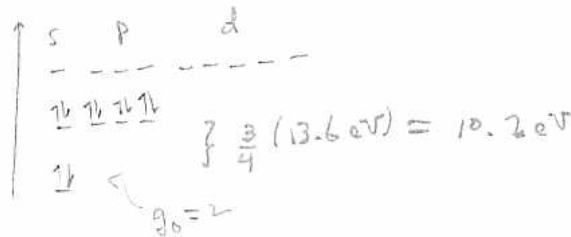
$$\langle E \rangle_{\text{classical}} = \frac{3}{2} RT \Rightarrow$$

$$k_B = \frac{R}{N_A}$$

② Stirling's Approx:  $\ln N! \approx N \ln N - N$  for  $N \gg 1$  ( $N \gtrsim 10$ )

so:  $\left( \frac{N}{e} \right)^N \approx N!$

③ electronic p.f.; E.g. H-atom

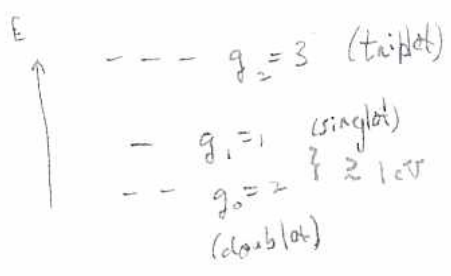


$$g_{\text{tot}} = \sum_j g_j e^{-\beta E_j}$$

[Energy levels]

⊖

Typically for molecules



usually

$$g_{\text{rel}} \approx g_0 e^{-\beta E_0}$$

since  $e^{-\beta(E_1 - E_0)} \approx e^{-\beta [1 \text{ eV}]}$

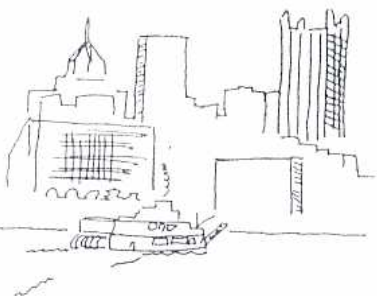
$$= e^{-\frac{8000}{200}} = 4.2 \times 10^{-18}$$

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assume  $\omega$  ~~unconnected~~ electronic g.s.  
connected!  
features



Sackur - Tetrode Eq. for

entropy of a mono atomic gas:

$$P = \left( \frac{g_{trans}}{h^3} \right)^3 \frac{N}{N!}$$

$$\langle E \rangle = \frac{3}{2} N k_B T + N \epsilon^{g.s.}$$

$$S = \frac{\langle E \rangle}{T} + k_B \ln P = \frac{3}{2} N k_B + k_B \ln \left\{ \left( \frac{g_{trans}}{h^3} \right)^3 \frac{N}{N!} \right\} \approx \frac{3}{2} N k_B + k_B \ln \left\{ \left( \frac{g_{trans} R}{N} \right)^3 \right\}$$

$$\ln N! = N \ln N - N$$

$$\left( \frac{N}{e} \right)^N = e^{N \ln N - N} \approx N! \quad \text{[Stirling]}$$

$$= \frac{3}{2} N k_B + N k_B \ln \left\{ \frac{g_{trans} \cdot e}{N} \right\}$$

$$= \frac{3}{2} N k_B + N k_B \ln \left( \frac{g_{trans}}{N} \right) = N k_B \ln \left\{ e^{3/2} \frac{g_{trans}}{N} \right\} \quad (1)$$

$$g_{trans} = \frac{4\pi V}{\Lambda^3}$$

$$\Lambda = \left( \frac{h^2}{2\pi m k_B T} \right)^{1/2}$$

Note: for ideal gas

$$P = \rho / k_B T$$

using fr. (1):  $\Lambda = 1.6 \times 10^{-9} \text{ cm}$

Example 19.7 Using the Sackur-Tetrode equation

Calculate the standard molar entropy of gaseous argon at 25°C.

Method. To calculate the molar entropy from eqn 32b we divide both sides by  $n$ . To calculate the standard molar entropy, we then set  $p = p^\ominus$ .

$$S_m^\ominus = R \ln \left( \frac{e^{3/2} k_B T}{p^\ominus \Lambda^3} \right)$$

Answer. The mass of an Ar atom is  $m = 39.95 \text{ u}$ . At 25°C, its thermal wavelength is 16.0 pm (by the same kind of calculation as in Example

19.4). Therefore,

$$S_m^\ominus = R \ln \left\{ \frac{e^{3/2} \times (4.12 \times 10^{-21} \text{ J})}{(10^5 \text{ N m}^{-2}) \times (1.60 \times 10^{-11} \text{ m})^3} \right\}$$

$$= 18.6R = 155 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$P = \frac{1 \text{ mol}}{22.4 \text{ l}} \times \frac{273}{300} \times 6.02 \times 10^{23} \times \frac{1 \text{ l}}{1000 \text{ cm}^3}$$

$$= 2.5 \times 10^{19} \frac{\text{atoms}}{\text{cm}^3}$$

thus:  $P \Lambda^3 = 1 \times 10^5 \Rightarrow \ln \left( e^{3/2} / P \Lambda^3 \right) = 18.6 \checkmark$



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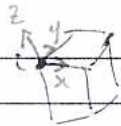
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Heat capacity of Crystals: Einstein model (1907)

Atoms in a 3-D lattice:



each atom vibrates in an effective isotropic force field  $V(x) = \frac{k}{2}(x^2 + y^2 + z^2)$  effective force constant.

thus  $C_v = 3N c_v$ ;  $c_v =$  heat capacity for 1-d harmonic oscillator w/  $\omega_0 = \sqrt{k/m}$

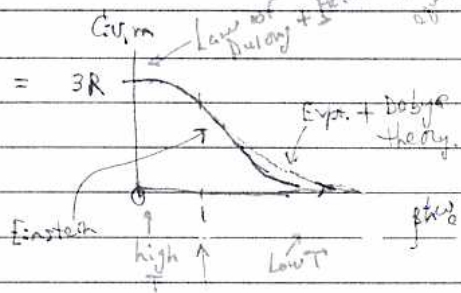
Einstein frequency of the crystal

$$c_v = \frac{d\langle E \rangle}{dT} = \frac{d}{dT} \left[ \frac{1}{2} k_B \coth\left(\frac{\beta \hbar \omega_0}{2}\right) \right] = k_B \frac{y^2}{\sinh^2(y)} \quad \left( y = \frac{\beta \hbar \omega_0}{2} \right)$$

[equivalent to classical at high T.]

thus, molar heat capacity of crystal is:

$$C_{v,m} = 3N_A k_B \frac{y^2}{\sinh^2(y)} = 3R$$



$\beta \hbar \omega_0 = 1 \Leftrightarrow$  cross-over from high T to low T.