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5.62 Physical Chemistry II
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5.62 Lecture #9: CALCULATION OF MACROSCOPIC PROPERTIES FROM MICROSCOPIC ENERGY LEVELS:

$$q_{\text{trans}}$$

The macroscopic thermodynamic properties are written in terms of Q . Q is related to the single-molecule partition function q , which is the sum over the molecular energy levels or states. Atoms and molecules have different kinds of states or energy levels. Each type of state makes its contribution, through q , to the macroscopic property under consideration.

TRANSLATIONAL CONTRIBUTION TO MACROSCOPIC PROPERTIES

Single-Molecule Translational Partition Function

$$q_{\text{trans}} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

Canonical Translational Partition Function

$$Q_{\text{trans}} = \frac{q_{\text{trans}}^N}{N!} = \frac{1}{N!} \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \right]^N$$

$$\begin{aligned} \ln Q_{\text{trans}} &= -\ln N! + N \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \right] \\ &= -N \ln N + N + \frac{3}{2} N \ln \left(\frac{2\pi mk}{h^2} \right) + \frac{3}{2} N \ln T + N \ln V \end{aligned}$$

($\ln N! = N \ln N - N$ is Stirling's Approximation)

Calculate the translational contribution to the average energy (one of the contributions to U , internal energy)

$$\begin{aligned} \bar{E} &= kT^2 \left(\frac{\partial \ln Q_{\text{trans}}}{\partial T} \right)_{N,V} \\ \left(\frac{\partial \ln Q_{\text{trans}}}{\partial T} \right)_{N,V} &= \frac{3}{2} \frac{N}{T} \end{aligned}$$

$$\bar{E} = kT^2 \left(\frac{3}{2} \frac{N}{T} \right) = \frac{3}{2} NkT = \frac{3}{2} nRT$$

Average translational energy of N molecules in a gas

What about the contribution of translational energy to the heat capacity

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_{N,V}$$

$$C_V^{\text{trans}} = \left(\frac{\partial \bar{E}_{\text{trans}}}{\partial T} \right)_{N,V} = \frac{\partial}{\partial T} \left[\frac{3}{2} NkT \right]$$

$$= \frac{3}{2} Nk = \frac{3}{2} nR$$

Recall from 5.60 that C_V for an ideal monatomic gas was often observed to be

$$\bar{C}_V = C_V / n = \frac{3}{2} R$$

There are no other important places other than translation for an ideal monatomic gas to put internal energy.

Calculate translational contribution to pressure :

$$p = - \left(\frac{\partial A}{\partial V} \right)_{N,T} = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} \quad (\text{recall } dA = -pdV - SdT + \mu dN)$$

because $A = -kT \ln Q$

$$\ln Q_{\text{trans}} = N \ln V + \ln \left(\frac{1}{N!} \right) + N \ln \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \quad (\text{only the first term is } V \text{ dependent})$$

$$\left(\frac{\partial \ln Q_{\text{trans}}}{\partial V} \right)_{N,T} = \frac{N}{V}$$

So

$$p = NkT/V$$

$$pV = NkT = nRT$$

IDEAL GAS LAW

Calculate translational contribution to entropy

$$S = k \ln Q + \bar{E}/T$$

$$\ln Q_{\text{trans}} = N \ln \left[\frac{(2\pi k)^{3/2}}{h^3} \right] + \frac{3}{2} N \ln m + \frac{3}{2} N \ln T + N \ln V - \ln N!$$

Again $\ln N! \sim N \ln N - N$ Stirling's approximation, which is valid for large N

$$\text{So } \ln Q_{\text{trans}} = N \left\{ \ln \left[\frac{(2\pi k)^{3/2}}{h^3} \right] + 1 + \frac{3}{2} \ln m + \frac{3}{2} \ln T + \ln \left(\frac{V}{N} \right) \right\}$$

$$\text{Now } \frac{V}{N} = \frac{kT}{p} \quad \therefore \ln \frac{V}{N} = \ln k + \ln T - \ln p$$

$$\text{So } \ln Q_{\text{trans}} = N \left[\ln \left[\frac{(2\pi)^{3/2} k^{5/2}}{h^3} \right] + 1 + \frac{3}{2} \ln m + \frac{5}{2} \ln T - \ln p \right]$$

$$S = k \ln Q + \frac{\bar{E}}{T} = k \ln Q + (3/2) Nk$$

$$S = Nk \left[\ln \left[\frac{(2\pi)^{3/2} k^{5/2}}{h^3} \right] + \frac{5}{2} + \frac{3}{2} \ln m + \frac{5}{2} \ln T - \ln p \right]$$

$$\frac{S}{Nk} = \frac{5}{2} \ln T + \frac{3}{2} \ln m - \ln p + \frac{5}{2} + \underbrace{\ln(\text{constants})}$$

$$\frac{S}{Nk} = \frac{5}{2} \ln T + \frac{3}{2} \ln m - \ln p - 1.164871$$

$$[T] = \text{K}; [m] = \text{g mol}^{-1}; \quad [p] = \text{atm (not S. I.)}$$

$$\boxed{S/Nk = \frac{5}{2} \ln T + \frac{3}{2} \ln m - \ln p - 1.15170} \quad [p] = \text{bar}$$

SACKUR-TETRODE EQUATION

1911-13

[Sackur and Tetrode were people, not equipment!]

P(ϵ) FOR TRANSLATIONWe know P_i for translation

$$P_i = P_{L,M,N} = \frac{e^{-\epsilon(L,M,N)/kT}}{q_{\text{trans}}}$$

↑
quantum
state

$$\text{where } \epsilon(L, M, N) = \frac{h^2}{8m} \left(\frac{L^2}{a^2} + \frac{M^2}{b^2} + \frac{N^2}{c^2} \right)$$

$$= \epsilon_x(L) + \epsilon_y(M) + \epsilon_z(N)$$

The lowest possible energy is for
 $L = M = N = 1$

probability of molecule in
 translational state with
 the three quantum
 numbers # L, M, N

But P(ϵ) is a more useful form than P_i .Rewrite $P_{L,M,N}$ as P(ϵ)

$$P(\epsilon) = \frac{g(\epsilon) e^{-\epsilon/kT}}{q_{\text{trans}}}$$

↑
prob. of
molecule
with energy ϵ

degeneracy (# of molecular
states with energy ϵ)

NEED: to calculate $g(\epsilon)$ Consider energy of N_2 molecule in state $L = 1, M = 1, N = 1$ in 10 cm cube.

$$\epsilon(1,1,1) = 3 \times 1.695 \times 10^{-20} \text{ kcal/mol} \quad (3 = 1 + 1 + 1)$$

Next higher energy state is

$$\epsilon(2,1,1) = 6 \times 1.695 \times 10^{-20} \text{ kcal/mol} \quad (6 = 4 + 1 + 1)$$

States are **very** close in energy: $\Delta\epsilon \approx 10^{-20}$ kcal/mol

Because the allowed energies of a molecule are so closely spaced, the discrete $P(\epsilon)$ can be approximated by a continuous $P(\epsilon) d\epsilon$. If $P(\epsilon)$ is treated as continuous, then $P_{L,M,N}$ must also be treated continuous because these distributions must map onto each other. The problem is more easily solved for 1 dimension at a time. Consider the x-dimension only

$P(\epsilon_x)d(\epsilon_x)$ represents probability of finding the molecule with energy between ϵ_x and $\epsilon_x + d\epsilon_x$ due to translation in the x direction; we want to determine this continuous distribution

$P(L)dL$ represents probability of finding the molecule with quantum number L between L and L + dL for motion in x-direction; we know this distribution by virtue of knowing the discrete distribution P_L

$$\frac{dL}{d\epsilon_x} = \frac{\# \text{ states between } L \text{ and } L + dL}{\epsilon_x(L + dL) - \epsilon_x(L)}$$

Often described as “# states per unit ϵ_x .”

$$P(L) = \frac{e^{-\epsilon_x(L)/kT}}{q_x} \quad \text{where } q_x = \left(\frac{2\pi mkT a^2}{h^2} \right)^{1/2} \quad \text{a is length of container in x direction}$$

$\underbrace{\hspace{10em}}_{\text{quantum number, not length}}$
 \downarrow

because

$$q_{\text{trans}} = q_x q_y q_z = \left(\frac{2\pi mkT a^2}{h^2} \right)^{1/2} \left(\frac{2\pi mkT b^2}{h^2} \right)^{1/2} \left(\frac{2\pi mkT c^2}{h^2} \right)^{1/2}$$

Now $P(\epsilon_x)$ and $P(L)$ are two continuous distribution functions which must map onto each other. In essence, they represent the same distribution but the variable has changed.

Problem is to relate $P(L)$ to $P(\epsilon_x)$. This can be done by

$$P(\epsilon_x)d\epsilon_x = P(L)dL$$

$$P(\epsilon_x) = P(L) \frac{dL}{d\epsilon_x}$$

Jacobian of the transformation
(see pages 9-7, 9-8 about the
change of variables)

The Jacobian for this change of variables is essentially the degeneracy. It tells us how many states there are within a small interval in ϵ_x ("density of states", dn/dE). [In quantum mechanics the density of states is also important. In one dimensional systems, it is proportional to the period of motion in a potential.]

Calculate $\frac{dL}{d\epsilon_x}$ so that $P(\epsilon_x)$ can be calculated

$$\epsilon_x = \frac{L^2 h^2}{8ma^2} \text{ or } L = \left(\frac{8ma^2 \epsilon_x}{h^2} \right)^{1/2}$$

so
$$\frac{dL}{d\epsilon_x} = \frac{d}{d\epsilon_x} \left(\frac{8ma^2 \epsilon_x}{h^2} \right)^{1/2} = \left(\frac{2ma^2}{h^2} \right)^{1/2} \epsilon_x^{-1/2}$$

so
$$P(\epsilon_x) = P(L) \frac{dL}{d\epsilon_x} = \frac{e^{-\epsilon_x(L)/kT}}{q_x} \left(\frac{2ma^2}{h^2} \right)^{1/2} \epsilon_x^{-1/2}$$

$$= \frac{e^{-\epsilon_x/kT}}{\left(\frac{2\pi mkT a^2}{h^2} \right)^{1/2}} \left(\frac{2ma^2}{h^2} \right)^{1/2} \epsilon_x^{-1/2}$$

$$P(\epsilon_x) = (\pi kT)^{-1/2} \epsilon_x^{-1/2} e^{-\epsilon_x/kT}$$

Check normalization (require $\int_0^\infty P(\epsilon_x) d\epsilon_x = 1$)

$$P(\epsilon_x) d\epsilon_x = \left(\frac{1}{\pi kT} \right)^{1/2} \epsilon_x^{-1/2} e^{-\epsilon_x/kT} d\epsilon_x$$

$$\int P(\epsilon_x) d\epsilon_x = \left(\frac{1}{\pi kT} \right)^{1/2} \frac{\pi^{1/2}}{(1/kT)^{1/2}} = 1$$

correctly normalized.

Therefore:

$$P(\epsilon_x) = (\pi kT)^{-1/2} \epsilon_x^{-1/2} e^{-\epsilon_x/kT}$$

BOLTZMANN KINETIC
ENERGY DISTRIBUTION
FUNCTION IN 1D

EXTREMELY IMPORTANT!

Probability of finding a free molecule in a gas with kinetic energy between ϵ_x and $\epsilon_x + d\epsilon_x$ due to translation in x-direction.

Note on Change of Variable(s)

For functions of one variable

We know $f(x)$ but we want to take the information contained in $f(x)$ and re-express it in terms of a different variable, y .

$$f(x)dx \equiv g(y)dy$$

We want to know $g(y)$ and know how to use it in place of $f(x)$.

$$dy = \frac{dy}{dx} dx$$

$$f(x)dx = g(y) \frac{dy}{dx} dx \text{ thus } f(x) = g[y(x)] \frac{dy}{dx}$$

and

$$g(y) = f[x(y)] \frac{dx}{dy}$$

$g[y(x)]$ means: evaluate the function $g(y)$ at the value of y determined by the value of the function $y(x)$ evaluated at x .

For functions of two or more variables

$$f(x, y, z, \dots) dx dy dz \dots = g(r, s, t, \dots) dr ds dt \dots$$

$$f(x, y, z, \dots) = \underbrace{\frac{\partial(r, s, t, \dots)}{\partial(x, y, z, \dots)}}_{\text{"Jacobian" of transformation}} g(r(x, y, z, \dots), s(x, y, z, \dots), t(x, y, z, \dots))$$

$$\frac{\partial(r, s, t, \dots)}{\partial(x, y, z, \dots)} = \begin{vmatrix} \frac{\partial r}{\partial x} & \frac{\partial s}{\partial x} & \frac{\partial t}{\partial x} & \dots & \dots \\ \frac{\partial r}{\partial y} & \frac{\partial s}{\partial y} & \frac{\partial t}{\partial y} & \dots & \dots \\ \frac{\partial r}{\partial z} & \frac{\partial s}{\partial z} & \frac{\partial t}{\partial z} & \dots & \dots \\ \cdot & \cdot & \cdot & \dots & \dots \\ \cdot & \cdot & \cdot & \dots & \dots \end{vmatrix}$$

where the single derivative for one variable is replaced by an $N \times N$ determinant of derivatives for N variables.

Example: $x, y, z, \leftrightarrow r, \theta, \phi$

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned}$$

3 x 3 determinant

$$dx dy dz = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial y}{\partial r} & \frac{\partial z}{\partial r} \\ \frac{\partial x}{\partial \theta} & \frac{\partial y}{\partial \theta} & \frac{\partial z}{\partial \theta} \\ \frac{\partial x}{\partial \phi} & \frac{\partial y}{\partial \phi} & \frac{\partial z}{\partial \phi} \end{vmatrix} dr d\theta d\phi = \begin{vmatrix} s\theta c\phi & s\theta s\phi & c\phi \\ r c\theta c\phi & r c\theta s\phi & -rs\theta \\ -rs\theta s\phi & rs\theta c\phi & 0 \end{vmatrix} dr d\theta d\phi$$

which reduces to the familiar result:

$$dx dy dz = r^2 \sin \theta \, dr d\theta d\phi.$$

A Note About Negative Temperature

We saw that the molecular partition function is

$$q = \sum_i e^{-\epsilon_i/kT}$$

and that the fractional population of the i -th level in one molecule is

$$\bar{f}_i = e^{-\epsilon_i/kT} / q$$

and the population of that level in a sample containing N molecules is

$$\bar{n}_i = N\bar{f}_i.$$

The population ratio for levels i and j

$$\frac{\bar{f}_i}{\bar{f}_j} = \frac{\bar{n}_i}{\bar{n}_j} = e^{-(\epsilon_i - \epsilon_j)/kT}$$

For $T > 0$.

When $\epsilon_i < \epsilon_j$, $\bar{f}_j < \bar{f}_i$

For $T \rightarrow 0K$ $\bar{f}_j \ll \bar{f}_i$

For $T \rightarrow \infty$ and $\epsilon_i < \epsilon_j$ $\bar{f}_j \approx \bar{f}_i$

But if $\bar{f}_j > \bar{f}_i$ (as occurs in a laser gain medium) that would imply $T < 0$.

There is no possibility of equilibrium with $T < 0K$, but one often uses a population ratio as a thermometer. Thus a “steady state” (but not equilibrium) situation is often described by a negative absolute temperature. Note that, if you started with a steady state sample at “ $T < 0K$ ”, and then turned off the source of energy input that sustains the nonequilibrium steady state, that “ T ” (defined by a population ratio) would become increasingly negative, pass through $-\infty$ directly to $+\infty$, and then decrease to the equilibrium T of the surroundings.