UNIT IIIC

MICROSCOPIC CALCULATION OF PERFECT GAS PROPERTIES

Statistical thermodynamics is a powerful tool for the determination of thermodynamic properties. The general technique requires selection of a model that describes the behavior of particles composing the system. Statistical procedures are then employed to predict thermodynamic properties. In this unit, we illustrate general techniques through application to molecular gas models. The numerical values of properties obtained by these procedures are of extreme practical significance. Equally important, however, is the physical insight provided by the form of the results and an understanding of the models upon which they are based.

Objectives

Upon concluding the unit the student should be able to:

1. Describe the indistinguishable limit and its significance in simplifying property determinations. Specify whether a given substance satisfies the indistinguishable limit at a specified thermodynamic state.

2. Differentiate between internal and external energy modes. Specify the relationship between the properties of each separate mode and those of the system as a whole.

3. Define the characteristic temperature for a model whose energy levels are specified as an analytic function.

4. Write the series definition of the partition function for a mode. Specify appropriate approximations for a mode partition function in the high- and low-temperature limits.

5. Derive an expression for a specified property from a given analytic expression for a mode's partition function.

6. Choose the correct number and types of modes for a specified molecule. Write an expression for its total properties and evaluate them at a specified state.

Supplementary References

1. Sonntag, R. E., and Van Wylen, G. J., <u>Introduction to Thermodynamics: Classical and Statistical</u>, Wiley (1971). Sects. 19.1 to 19.9 with Exmps. 19.1 to 19.7, and Exers. 19.1 to 19.35. Similar to this unit. A good supplement. Also, Chapter 18 provides a much more thorough treatment of the quantum mechanical principles underlying statistical mechanics with emphasis on the models employed in this unit.

2. Wark, K., <u>Thrmodynamics</u>, Second Ed., McGraw-Hill (1971). Sects. 10-7 to 10-15 with Exmps. 10-1 to 10-2 and Exers. 10-6 to 10-35. A brief but clear treatment that excludes polyatomic gases.

3. Holman, J. P., <u>Thermodynamics</u>, Second Ed., McGraw-Hill (1974). Sects. 8.2 to 8.5 with Exmps. 8-1 and 8-2 and Exers. 8-1 to 8-3, 8-8 to 8-13 and 8-16. Excludes polyatomic gases. Quite brief, a quick overview.

CONTENTS

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Precise thermodynamic calculations are dependent on the availability of accurate property
data. Macroscopic property measurement to obtain these data has two serious drawbacks.
One, accurate measurements are difficult, and therefore expensive. Two, the results are
limited to the range covered by the measurements. Hence, many data points must be col-
lected to cover a broad range. This unit introduces an alternative, microscopic, property
determination procedure that overcomes both of these limitations.

The microscopic approach predicts properties on the basis of a model of individual
particle behavior. Each model requires as input certain *particle characteristics*, e.g.,
mass, moment of inertia, the effective spring constant of the molecular bonds, etc. These
parameters are *inferred* from measurement, usually from the emission spectra of the sub-
stance. Since the parameters are molecular constants, a single set is sufficient for each
substance, and the analytical relationship between the model and the properties consti-
tutes an extrapolation over a range of thermodynamic states. Thus the microscopic method
doesn't simply produce required data. Its requirement that a molecular model be selected
provides valuable understanding of how and why properties vary and when they can be ex-
pected to be constant. This perception can contribute significantly to engineering
judgement.

In this unit we use the microscopic procedure to predict the properties of indepen-
dent particle molecular gases. We will find that when gaseous particles are independent
they fall within the perfect gas region. Further, gaseous system particles are indistin-
guishable. They obey either Bose-Einstein or Fermi-Dirac statistics depending upon whether
they have an even or an odd number of subatomic components. In general, the properties of
Bosons and Fermions are distinct (Unit IIID). But there is an asymptotic limit in which
the fundamental basis of their difference, the Pauli exclusion principle (Unit IIIA), is
inconsequential. In this limit the properties of Bosons and Fermions are the same. We
will see below that for gases whose particles are atoms or molecules (as opposed to elec-
trons or electromagnetic and acoustic waves) the limit is satisfied under almost all
achievable conditions. Therefore, this unit considers the properties of molecular perfect
gases only in the indistinguishable limit.

I.   THE INDISTINGUISHABLE LIMIT

In Unit IIIB we developed the equilibrium distribution function for the distinguish-
able particles, Boltzons, as well as for the indistinguishable Fermions and Bosons

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$$n_j^{MB} = \frac{g_j}{e^{[\alpha+\varepsilon_j(V)]/kT}} \qquad n_j^{FD} = \frac{g_j}{e^{[\alpha+\varepsilon_j(V)]/kT}+1} \qquad n_j^{BE} = \frac{g_j}{e^{[\alpha+\varepsilon_j(V)]/kT}-1} \qquad (IIIB-8,14,16)$$

Inspection reveals that these forms differ by a single term, namely, the +1, -1, or 0 appearing in the denominator. Therefore the two indistinguishable particle distribution functions become identical to one another and to the distinguishable particle, Maxwell-Boltzmann distribution function in the limit $e^{[\alpha+\varepsilon_j(V)]/kT} \gg 1$. This limit, called the *indistinguishable* or the Boltzmann *limit* (*il*), is described by the condition $n_j \ll g_j$.

Recall that the distinction between Fermions and Bosons results from the Pauli exclusion principle. (No more than one Fermion can occupy a state, $n_j^{FD} < g_j$; but any number of Bosons can.) But the indistinguishable limit is $n_j \ll g_j$. Therefore, in this limit very few states would contain more than one Boson and the effect of the Pauli exclusion principle on the distribution is inconsequential. This provides a physical explanation for the fact that $n_j^{FD} \simeq n_j^{BE} = n_j^{il}$ when $n_j \ll g_j$. The following example provides an analytic explanation.

Example 1. Use the condition $n_j \ll g_j$ to establish a relationship between the number of microstates in a macrostate, W_i, for indistinguishable Fermions and Bosons to that of distinguishable Boltzons valid in the indistinguishable limit.

Eqns. IIIA-7a, b and c give the relationships between $n_{j,i}$, g_j and W_i. For Fermions it is $W_i^{FD} = \prod_j g_j!/[(g_j-n_{j,i})!n_{j,i}!]$. To establish its value in the limit, examine the ratio

$$\frac{g_j!}{(g_j-n_{j,i})!} = \frac{g_j(g_j-1)(g_j-2)\cdots(g_j-n_{j,i}+2)(g_j-n_{j,i}+1)(g_j-n_{j,i})!}{(g_j-n_{j,i})!}$$

But in the limit $n_{j,i} \ll g_j$, $\qquad\qquad g_j \simeq (g_j-1) \simeq \cdots \simeq \cdots \simeq (g_j-n_{j,i}+1)$

So

$$\frac{g_j!}{(g_j-n_{j,i})!} \simeq g_j^{n_{j,i}} \qquad \text{and} \qquad W_i^{FD} \Rightarrow \prod_j \frac{g_j^{n_{j,i}}}{n_{j,i}!}$$

The expression for Bosons is $W_i^{BE} = \prod_j (g_j+n_{j,i}-1)!/[(g_j-1)!n_{j,i}!]$. Using the same approach, examine

$$\frac{(g_j+n_{j,i}-1)!}{(g_j-1)!} = \frac{(g_j+n_{j,i}-1)(g_j+n_{j,i}-2)\cdots g_j(g_j-1)!}{(g_j-1)!}$$

But in the limit $n_{j,i} \ll g_j$ $\qquad\qquad (g_j+n_{j,i}-1) \simeq (g_j+n_{j,i}-2) \simeq \cdots \simeq g_j$

So

$$\frac{(g_j+n_{j,i}-1)!}{(g_j-1)!} \simeq g_j^{n_{j,i}} \qquad \text{and} \qquad W_i^{BE} \Rightarrow \prod_j \frac{g_j^{n_{j,i}}}{n_{j,i}!}$$

Further for Boltzons, $W_i^{MB} = N! \prod_j \left(g_j^{n_{j,i}}\right)/n_{j,i}!$. Thus when $n_{j,i} \ll g_j$, $W_i^{FD} \Rightarrow W_i^{BE} \Rightarrow W_i^{MB}/N!$

... example showed that in the indistinguishable limit the number of microstates
...ate is the same for Fermions and Bosons. But it is smaller than that for .
... factor of $N!$[1]

...recognized that the distribution of particles over the levels is the same for
...atistics in the Boltzmann limit, we can borrow the expression for α obtained
...ns in Unit IIIB, $e^{\alpha} = Z(T,V)/N$, where $Z = \sum_{j=1} g_j \exp\left[-\varepsilon_j(V)/kT\right]$. This gives
...rium distribution and equivalently the probability that a particle will be in
...vel in the limit $n_j \ll g_j$.

$$n_j = n_j^{MB} = \frac{Ng_j e^{-\varepsilon_j(V)/kT}}{Z(T,V)} \qquad \rho_j^{i\ell} = \rho_j^{MB} = \frac{n_j}{N} = \frac{g_j e^{-\varepsilon_j(V)/kT}}{Z(T,V)} \qquad \text{(IIIC-1a,b)}$$

...e distribution functions become the same in the limit, the entropy of indistin-
... Bosons and Fermions remains distinct from that of distinguishable Boltzons. The
...: a macrostate was defined by eqn. IIIB-1 ($S_i \equiv k\ell n W_i$). This is applicable to
...: statistics. Thus, using the result of Exmp. 1 we have

$$S^{MB} = k\ell n W^{MB} \qquad S^{i\ell} = k\ell n\left(\frac{W_{MB}}{N!}\right) = S^{MB} - k\ell n N!$$

...ibrium entropy of a system of Boltzons was formulated in Unit IIIB as

$$S^{MB} = \frac{U}{T} + Nk\ell n[Z(T,V)] \qquad \text{(IIIB-13)}$$

...substitute this result and Stirling's approximation ($\ell n N! = N\ell n N - N$, see Appendix
...-A), we obtain

$$S^{i\ell} = \frac{U}{T} + Nk\ell n\left[\frac{Z(T,V)}{N}\right] + Nk$$

...e relationships provide the basis for the determination of the properties of Boltzons,
... those of Fermions and Bosons in the indistinguishable limit. Microscopic property
...rmination capitalizes on the similarity between substances. It is therefore conven-
...t to formulate properties in *molar units*. We do so by substituting $nN_A = N$ and $n\bar{v} = V$.
...s gives (note that $N_A k = \bar{R}$)

$$\bar{n}_j = \frac{n_j}{n} = \frac{N_A g_j e^{-\varepsilon_j(n\bar{v})/kT}}{Z(T,n\bar{v})} \qquad \text{(IIIC-1a)}$$

$$\bar{s}^{MB} = \frac{\bar{u}}{T} + \bar{R}\ell n[Z(T,n\bar{v})] \qquad \bar{s}^{i\ell} = \frac{\bar{u}}{T} + \bar{R}\ell n\left[\frac{Z(T,n\bar{v})}{nN_A}\right] + \bar{R} \qquad \text{(IIIC-2a,b)}$$

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[1] $N!$ is the number of permutations, or distinct rearrangements, of N items. This is
often advanced as a physical interpretation of the appearance of that factor. However it
is not an acceptable argument as the $n_j!$ which appears in the denominator of all three
statistical formulae also has its origin in the distinguishability characteristic. It
appears in the Boltzon expression, so that the order in which the distinguishable par-
ticles are placed in the levels is not counted. And it appears in the Bose and Fermi ex-
pressions to discount the counting of arrangements of the indistinguishable particles
among the states in the levels. (See Ref. 4, pg 140.)

The partition function is applicable to Boltzons and to Bosons and Fermions in the indistinguishable limit. It appears in each of the above expressions. The effort required to evaluate properties is greatly reduced if we formulate all properties in terms of the partition function and its derivatives.[2]

and

$$\left[\frac{\partial Z(T,n\bar{v})}{\partial T}\right]_{\bar{v}} = \sum_{j=1}^{J} g_j\left[\frac{\varepsilon_j(n\bar{v})}{kT^2}\right]e^{-\varepsilon_j(n\bar{v})/kT} = -\frac{1}{kT^2}\sum_{j=1}^{J} g_j\varepsilon_j(n\bar{v})e^{-\varepsilon_j(n\bar{v})/kT}$$

$$\left[\frac{\partial Z(T,n\bar{v})}{\partial \bar{v}}\right]_{T} = \sum_{j=1}^{J} g_j\left[-\frac{1}{kT}\frac{\partial\varepsilon_j(n\bar{v})}{\partial\bar{v}}\right]e^{-\varepsilon_j(n\bar{v})/kT} = -\frac{n}{kT}\sum_{j=1}^{J} g_j\left[\frac{d\varepsilon_j(n\bar{v})}{d(n\bar{v})}\right]e^{-\varepsilon_j(n\bar{v})/kT}$$

With these functions we can recognize the correspondence of properties to the partition function from their definitions.

1. Internal Energy is defined as

$$\bar{u} = \sum_{j=1}^{J} n_j\varepsilon_j(n\bar{v}) = \frac{N_A}{Z(T,n\bar{v})}\sum_{j=1}^{J} g_j\varepsilon_j(n\bar{v})\,e^{-\varepsilon_j(n\bar{v})/kT}$$

Examining the form of $(\partial Z/\partial T)_{\bar{v}}$, we see that $\bar{u} = (N_A kT^2/Z)(\partial Z/\partial T)_{\bar{v}}$ or

$$\bar{u} = \frac{\bar{R}T^2}{Z}\left[\frac{\partial Z(T,n\bar{v})}{\partial T}\right]_{\bar{v}} = \bar{R}T^2\left[\frac{\partial \ln Z(T,n\bar{v})}{\partial T}\right]_{\bar{v}} \qquad (IIIC\text{-}3)$$

2. Entropy. With the development of eqn. IIIC-3 the entropy can be written in terms of the partition function

$$\bar{s}^{MB} = \bar{R}T\left[\frac{\partial \ln Z(T,n\bar{v})}{\partial T}\right]_{\bar{v}} + \bar{R}\ln Z(T,n\bar{v}) \qquad (IIIC\text{-}4a)$$

$$\bar{s}^{il} = \bar{R}T\left[\frac{\partial \ln Z(T,n\bar{v})}{\partial T}\right]_{\bar{v}} + \bar{R}\ln\left[\frac{Z(T,n\bar{v})}{nN_A}\right] + \bar{R} \qquad (IIIC\text{-}4b)$$

3. Pressure was defined in terms of microscopic parameters in Unit IIIB (see footnote 15)

$$p = -\sum_{j=1}^{J} n_j\frac{d\varepsilon_j(V)}{dV} = \frac{nN_A}{Z}\sum_{j=1}^{J} g_j\left[\frac{d\varepsilon_j(n\bar{v})}{d(n\bar{v})}\right]e^{-\varepsilon_j(n\bar{v})/kT}$$

Examining the form of $(\partial Z/\partial\bar{v})_T$, we see that

$$p = \frac{\bar{R}T}{Z}\frac{\partial Z}{\partial\bar{v}}\bigg|_T = \bar{R}T\left[\frac{\partial \ln Z(T,n\bar{v})}{\partial\bar{v}}\right]_T \qquad (IIIC\text{-}5)$$

4. Enthalpy. Substitution of eqns. IIIC-3 and IIIC-5 into the definition of enthalpy yields

$$\bar{h} = \bar{u} + p\bar{v} = \bar{R}T\left[T\left(\frac{\partial \ln Z}{\partial T}\right)_{\bar{v}} + \bar{v}\left(\frac{\partial \ln Z}{\partial\bar{v}}\right)_T\right] \qquad (IIIC\text{-}6)$$

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[2] All derivatives are performed at a fixed number of moles. The subscript n is implicit.

5. <u>Constant Volume Specific Heat</u>, c_v is obtained by differentiating eqn. IIIC-3[3]

$$\bar{c}_v = \left(\frac{\partial \bar{u}}{\partial T}\right)_{\bar{v}} = \left[\frac{\partial}{\partial T}\ \bar{R}T^2\left(\frac{\partial \ln Z}{\partial T}\right)_{\bar{v}}\right]_{\bar{v}} = 2\bar{R}T\left(\frac{\partial \ln Z}{\partial T}\right)_{\bar{v}} + \bar{R}T^2\left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_{\bar{v}} \qquad \text{(IIIC-7)}$$

The above relationships demonstrate that if the partition function can be formulated analytically as a function of T and $\bar{v}$, the macroscopic properties are readily obtained. Therefore, microscopic determination of the properties of Boltzons, Bosons and Fermions in the indistinguishable limit reduces to finding $Z(T,\eta\bar{v})$.

II. EVALUATION OF THE PARTITION FUNCTION

The partition function is defined as the sum over the J levels, or equivalently P states, accessible to the particles composing the system.

$$Z(T,\eta\bar{v}) = \sum_{j=1}^{J} g_j e^{-\epsilon_j(\eta\bar{v})/kT} = \sum_{p=1}^{P} e^{-\epsilon_p(\eta\bar{v})/kT} \qquad \text{(IIIB-12)}$$

Example 2. Consider a system with a triply degenerate first level, $g_1 = 3$. Expand the first three terms of the sum over states and show that the result is equivalent to the first term of the sum over levels.

$$Z = \sum_{p=1}^{P} e^{-\epsilon_p/kT} = e^{-\epsilon_{p=1}/kT} + e^{-\epsilon_{p=2}/kT} + e^{-\epsilon_{p=3}/kT} + \sum_{p=4}^{P} e^{-\epsilon_p/kT}$$

The first three states of this series are members of the same level, so $\epsilon_{p=1} = \epsilon_{p=2} = \epsilon_{p=3} = \epsilon_{j=1}$, $g_{j=1} = 3$. Thus the first terms can be written

$$Z = 3e^{-\epsilon_{j=1}/kT} + \sum_{p=4}^{P} e^{-\epsilon_p/kT}$$

The remainder of the series, beginning at $p = 4$, can be rewritten in terms of levels beginning at $j = 2$. States of equal value can be collapsed in an analogous manner with the degeneracy of each level. Thus

$$Z = 3e^{-\epsilon_{j=1}/kT} + \sum_{j=2}^{J} g_j e^{-\epsilon_j/kT} = \sum_{j=1}^{J} g_j e^{-\epsilon_j/kT}$$

We thus see the equivalence of the two series formulations.

As written, the series of energy levels accounts for all contributions to the particle energy. In the evaluation of the partition function it is useful to subdivide particle energy into components.

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[3]The specific heat at constant pressure can be formulated in an analogous manner, using direct integration of eqn. IIIC-6, $\bar{c}_p = (\partial\bar{h}/\partial T)_p$. But the constant pressure condition is not easily applied. It is far easier to determine $\bar{c}_p$ from $\bar{c}_v$ using eqn. ID-6, $\bar{c}_p - \bar{c}_v = Tv\beta^2/\kappa$. For a perfect gas, $\bar{c}_p^* = \bar{c}_v^* + \bar{R}$.

A. External and Internal Energy Modes

We begin the division into components by separating the energy which is dependent on the internal structure of the particle, *internal modes*, from that which is not, the *external mode*. The energy of the external mode includes the kinetic energy contribution of center of gravity translation and the potential energy contribution due to interparticle forces. This unit is restricted to consideration of systems of *identical nonlocalized particles*, liquids or gases; that is, to systems of indistinguishable Bosons or Fermions and these only in the Boltzmann limit.[4] In addition, all of Units III are limited to independent particles (see Unit IIIA, Sect. IIA). To be considered independent nonlocalized particles must have negligible interparticle forces. Thus, the only external mode contribution to be considered is that of translation. The only phase to be considered is the gas phase.[5]

The principal advantage of separating energy into modes is that the energy levels and degeneracies (ε_j and g_j) of complex particles can be evaluated one mode at a time. Separation into modes allows the external mechanics of translation to be uncoupled from the internal particle mechanics. That is, the solution of the Schroedinger equation for independent particle translation— the particle in a box (Unit IIIA)— can be used in combination with separately obtained Schroedinger equation solutions for the internal modes. The total wave function can then be determined from $\psi = \psi_{ex}\psi_{in}$. The degeneracy is simply the number of distinct wave functions, that is, states that have the same energy. Thus, the degeneracy follows the same product rule as the wave function. The separate mode energy levels are additive.

$$g_{j(i,\ell)} = g_{ex,i}g_{in,\ell} \qquad \varepsilon_{j(i,\ell)}(n\bar{v}) = \varepsilon_{ex,i}(n\bar{v}) + \varepsilon_{in,\ell} \qquad \text{(IIIC-8a,b)}$$

The level designation, j, refers to the total mechanics of the particle. The separate modes have been ordered into levels in an analogous manner. Their index designations are i and ℓ. Therefore, the net level sequence is dependent on each subsequence, $j(i,\ell)$. Using eqns. IIIC-8a,b the total partition function becomes

$$Z(T,\bar{v}) = \sum_{j=1}^{J} g_{j(i,\ell)} e^{-\varepsilon_{j(i,\ell)}(n\bar{v})/kT} = \sum_{i=1}^{I} \sum_{\ell=1}^{L} g_{ex,i}g_{in,\ell} e^{-[\varepsilon_{ex,i}(n\bar{v}) + \varepsilon_{in,\ell}]/kT}$$

$$= \sum_{i=1}^{I} g_{ex,i} e^{-\varepsilon_{ex,i}(n\bar{v})/kT} \cdot \sum_{\ell=1}^{L} g_{in,\ell} e^{-\varepsilon_{in,\ell}/kT} = Z_{ex}(T,n\bar{v})Z_{in}(T) \qquad \text{(IIIC-9)}$$

Similarly, the probability distribution can be formulated as

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[4]Boltzons are also identical particles. Identical particles become distinguishable when they are tied to specific positions in a lattice.

[5]The translating particles in a liquid interact with one another. They are dependent.

$$\rho_{j(i,\ell)} = \frac{g_{j(i,\ell)} e^{-\varepsilon_{j(i,\ell)}(n\bar{v})/kT}}{Z(T,n\bar{v})} = \frac{g_{ex,i} g_{in,\ell} e^{-[\varepsilon_{ex,i}(n\bar{v}) + \varepsilon_{in,\ell}]/kT}}{Z_{ex}(T,n\bar{v}) \, Z_{in}(T)}$$

$$= \rho_{ex,i}(T,n\bar{v}) \, \rho_{in,\ell}(T) \tag{IIIC-10}$$

That is, the probability that a particle will be in the $j(i,\ell)^{th}$ level is the product of the probabilities that it will be in the ith external level and the ℓth internal level.[6] Notice that only the external mechanics of the particle is dependent on the system volume. (The volume enters the solution of the Schroedinger equation through the boundary conditions.) Therefore, *only the external energy levels and partition function are dependent on the system volume.*

Separation of the partition function into modes allows properties to be determined for each separate mode. Specifically since the partition function appears in property relationships as a logarithm (eqns. IIIC-3 to 7), its contributions are additive, $\ell n[Z(T,n\bar{v})] = \ell n[Z_{ex}(T,n\bar{v})] + \ell n[Z_{in}(T)]$. As applied in eqns. IIIC-3 to 7, we have

$$\bar{u} = \bar{u}_{ex} + \bar{u}_{in} \qquad \bar{c}_v = \bar{c}_{v,ex} + \bar{c}_{v,in}$$

$$p = p_{ex} + p_{in} \qquad \bar{h} = \bar{u}_{ex} + p_{ex} \cdot \bar{v} + \bar{u}_{in}$$

We can use the same approach with the entropy. The results are identical when applied to Boltzons, eqn. IIIC-2a.

$$\bar{s}^{MB} = \bar{s}_{ex}^{MB} + \bar{s}_{in}^{MB} = \left(\frac{\bar{u}_{ex}}{T} + \bar{R}\ell n Z_{ex}\right) + \left(\frac{\bar{u}_{in}}{T} + \bar{R}\ell n Z_{in}\right)$$

But when we apply this principle in the indistinguishable limit, the term that comes from N! (see Exmp. 1) must be included in the entropy; but only once. We therefore define the external and internal entropy components in the indistinguishable limit as

$$\bar{s}^{i\ell} = \bar{s}_{ex}^{i\ell} + \bar{s}_{in}^{i\ell} \qquad \bar{s}_{ex}^{i\ell} = \frac{\bar{u}_{ex}}{T} + \bar{R}\ell n\left(\frac{Z_{ex}}{n N_A}\right) + \bar{R} \qquad \bar{s}_{in} = \frac{\bar{u}_{in}}{T} + \bar{R}\ell n Z_{in} \tag{IIIC-11a,b,c}$$

We have found that separate determination of $Z_{ex}(T,n\bar{v})$ and $Z_{in}(T)$ is sufficient to determine indistinguishable limit properties. In this case the energy levels and degeneracies of the *external* mode are those of the *particle in the box*, Unit IIIA. The physical mechanisms that contribute to the internal modes include:

1. <u>Rotation</u> of the particle about its center of gravity; 2. <u>Vibration</u> of the constituent atoms about their mean position in the molecule; 3. Excitation of bound electrons into higher <u>electronic</u> levels or, at higher energies, release of the intermolecular binding potential when atoms are <u>dissociated</u> from the particle, or, at still higher energies, release bound electrons from the particle, <u>ionization</u>; 4. Rotation of the nucleus about a <u>nuclear spin</u> axis.

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[6]The distribution function for the number of particles per level, n_j, cannot be written analogously. $n_{j(i,\ell)} \neq n_{ex,i} n_{in,\ell}$. Rather $n_{j(i,\ell)} = N \rho_{ex,i} \rho_{in,\ell}$.

In most cases these internal mechanisms are independent, exceptions are noted below. When this is the case, the internal mode can be further subdivided into separate contributions and by analogy with eqn. IIIC-8, we have

$$Z_{in}(T) = Z_r(T) \, Z_v(T) \, Z_{el}(T) \, Z_n(T)$$

As before when the partition function is a product we can write the properties as a sum over the separate modes ($p_{in} = 0$).

$$\bar{u}_{in} = \bar{u}_r + \bar{u}_v + \bar{u}_{el} + \bar{u}_n \qquad\qquad \bar{c}_{v,in} = \bar{c}_{v,r} + \bar{c}_{v,v} + \bar{c}_{v,el} + \bar{c}_{v,n}$$

$$\bar{s}_{in} = \bar{s}_r + \bar{s}_v + \bar{s}_{el} + \bar{s}_n$$

This places even more stress on the determination of the partition functions.

B.   The Characteristic Temperature of a Mode

The solution of the Schroedinger equation for each independent mode yields its energy levels, viz., for the pth mode, $\varepsilon_{p,\ell}$, and degeneracy, $g_{p,\ell}$. When these input data are available the mode partition function is determined in principle.

$$Z_p = \sum_{\ell=1}^{L} g_{p,\ell} \, e^{-\varepsilon_{p,\ell}/kT} \qquad\qquad (IIIB-11)$$

In most physical systems, including all of the modes we will investigate, $L = \infty$. Hence, eqn. IIIB-11 is an infinite series. The practicality of using direct summation to evaluate such series is governed by its rate of convergence. Moreover, the partition function has little value in itself. Its value is its relationship to properties. These require that one take its logarithm and derivative. It is, therefore, *highly advantageous that the partition function be expressed as an analytical function.* Circumstances for which the partition function can be so expressed are:

1.   Exact Series: In at least one important case, the vibrational mode, the series representation reduces exactly to a transcendental function. In such cases general analytical expressions for the property contribution of that mode can be obtained.

2.   Low-Temperature Limit: The sum over levels is arranged in the order of increasing energy, $\varepsilon_{p,1} < \varepsilon_{p,2} < \varepsilon_{p,3}$, etc. If the temperature satisfies the condition $(\varepsilon_{p,2} - \varepsilon_{p,1})/kT \gg 1$ the series converges rapidly and is adequately represented by a few, often one or two terms.

$$Z_p(T) \simeq g_{p,1} \, e^{-\varepsilon_{p,1}/kT} + g_{p,2} \, e^{-\varepsilon_{p,2}/kT}$$

3.   High-Temperature Limit: If the spacing between the adjacent energy levels is small, $(\varepsilon_{p,\ell+1} - \varepsilon_{p,\ell})/kT \ll 1$, then the rate of convergence of the series is slow and it can be represented by an integral.

$$Z_p = \sum_{\ell=1}^{L} g_{p,\ell} \, e^{-\varepsilon_{p,\ell}/kT} \approx \int_{\ell=1}^{L} g_p(\ell) e^{-\varepsilon_p(\ell)/kT} \, d\ell = \int_{\varepsilon_{p,min}}^{\varepsilon_{p,max}} g_p(\varepsilon_p) e^{-\varepsilon_p/kT} \, d\varepsilon_p$$

Note that if one is to use the first integral representation both, the degeneracy and the energy must be expressed in closed form as a function of the level index, $g_{p,\ell} \rightarrow g_p(\ell)$ and $\varepsilon_{p,\ell} \rightarrow \varepsilon_p(\ell)$. And if the second integral representation is to be used the degeneracy must be expressed as a function of the energy, $g_{p,\ell} \rightarrow g_p(\varepsilon_\ell)$.

Referring to the first of the preceding three possibilities, when the series is exact, e.g., the vibrational model, representation as a transcendental function is the preferred evaluation method. The last two methods are asymptotic temperature limits that exist for all modes. They are important not only for their analytic simplification, but also for their physical significance. *In its low-temperature limit a mode is unexcited.* It then contributes no more than a constant to properties. (The constant is frequently zero.) *In the high-temperature limit a mode is fully excited.* It is interesting to note that discreteness of the energy spectrum is central to the low-temperature asymptote (this is the quantum limit). But in the high-temperature limit energy can be viewed as continuous; this is the classical, or Newtonian limit.

Each mode has its own limits. (A high temperature to one mode may be low to another.) Therefore, the most significant characteristic for each mode is the parameter that discriminates between its high and low temperature limits. This parameter is identified by noting that the quantized energy levels can always be expressed in the form

$$\varepsilon_{p,\ell} = B_p f_p(\ell) \qquad \text{(IIIC-12)}$$

in which $f_p(\ell)$ is a dimensionless function of the level index, ℓ (or equivalently of the quantum numbers). Since the index is the positive integer series, $f_p(\ell)$ is a discontinuous function; it expresses the quantization of energy. The coefficient B_p has dimensions of energy. It contains the physical characteristics of the mode. We will find that the incremental changes in the quantum index function $f_p(\ell)$ are of order one, $f_p(\ell+1) - f_p(\ell) \sim 0(1)$. Therefore, it is B_p that discriminates between the mode's high and low temperatures. The physical significance of B_p is more recognizable if its values are reported with dimensions of temperature. The *characteristic temperature* of a mode is defined as

$$\theta_p \equiv \frac{B_p}{k} \qquad \text{(IIIC-13)}$$

<u>Exercise 1.</u> The energy states for the particle in a box, translation of an independent particle, were found to be

$$\varepsilon_{tr}(\ell,m,n) = \frac{h^2}{8m^*v^{2/3}} (\ell^2 + m^2 + n^2)$$

where $\ell, m, n = 1, 2, 3, \ldots$. Identify the discrete dimensionless function of the quantum numbers $f_{tr}(\ell,m,n)$, the physical coefficient B_{tr} and the characteristic temperature θ_{tr} for this mode.

Since we will use values of the characteristic temperature to describe the properties of each substance in each mode, it is convenient to formulate the partition function and

its limits explicitly in terms of θ_p. In this form the general series is

$$Z_p = \sum_{\ell=1}^{L} g_{p,\ell}\, e^{-[f_p(\ell)\theta_p]/T} \qquad\qquad \text{(IIIC-14a)}$$

And the low- and high-temperature limits are

$$Z_p\Big|_{T<<\theta_p} = g_{p,1}\, e^{-[f_p(1)\theta_p]/T} + g_{p,2}\, e^{-[f_p(2)\theta_p]/T} \qquad\qquad \text{(IIIC-14b)}$$

$$Z_p\Big|_{T>>\theta_p} = \int_{\ell=1}^{L} g_p(\ell)\, e^{-[f(\ell)\theta_p]/T}\, d\ell \qquad\qquad \text{(IIIC-14c)}$$

These relationships are applied to the external and internal modes of gaseous particles in the following section.

III. THE CHARACTERISTICS OF ENERGY MODES

The characteristics of independent indistinguishable particles can be separated into a single external and several internal modes. In this section we develop expressions for their individual partition functions and property contributions. We begin with the external mode.

A. The External (Translational) Mode

The external energy of independent, indistinguishable particles results from translation. The quantum mechanics of independent particle translation were treated in Unit IIIA. In the form of eqns. IIIC-12 and 13 (see Exer. 1) the translational energy states are

$$\varepsilon_{tr}(\ell,m,n) = k\theta_{tr}(m^*,V) \cdot f(\ell,m,n)$$

where $\qquad \theta_{tr}(m^*,V) = \dfrac{h^2}{8m^* V^{2/3} k} \qquad f(\ell,m,n) = (\ell^2 + m^2 + n^2) \qquad \ell,m,n = 1,2,3,\ldots,$

Notice that $\theta_{tr}(m^*,V)$ is dependent on the mass of the translating particles and the extensive volume of their container (not the molar volume). To establish a quantitative feel for the range of validity of the high and low temperature limits of this mode consider the following example.

Example 3. Determine the magnitude of θ_{tr} for nitrogen gas in a 30 m^3 room. Particle mass is determined from definition 7 of Unit IA.

$$m^* = \frac{M}{N_A} = \frac{28.1 \text{ kg/(kg mol)}}{6.023 \cdot 10^{26}\text{part/(kg mol)}} = 4.649 \cdot 10^{-26}\text{kg/part}$$

Thus the characteristic temperature is (see Table IA-2 for the required physical constants)

$$\theta_{tr} = \frac{h^2}{8m^* V^{2/3} k} = \frac{(6.625 \cdot 10^{-34}\text{Js/part})^2 \cdot 1 \text{ kg m}^2/(\text{Js}^2)}{8 \cdot 4.649 \cdot 10^{-26}\text{kg/part } (30 \text{ m}^3)^{2/3} \cdot 1.38 \cdot 10^{-23}\text{J/(part K)}} = 8.857 \cdot 10^{-21}\text{K}$$

Exmp. 3 demonstrates that θ_{tr} is extremely small for nitrogen molecules in a room size

container. Notice that small values of particle mass and container volume tend to increase θ_{tr}. The following exercise investigates the limit.

Exercise 2. Hydrogen is the lightest pure substance. Determine the volume of a hydrogen container which would be required to achieve a value of θ_{tr} as high as the lowest temperatures that have been achieved in the laboratory, $\sim 10^{-6}$ K.

The preceding problems demonstrate that gases composed of *atomic size particles are always in the high-temperature translational limit,* $T \gg \theta_{tr}$.[7] Thus, it is only necessary to evaluate Z_{tr} for this limit. Application of eqn. IIIC-14c requires that the degeneracy be expressed as an analytic function of the level index, $g_{tr}(\ell)$. But the translational energy magnitudes have so far been written in terms of state designation, i.e., the quantum numbers. Thus, we must either transform eqn. IIIC-14c to an integral over the states or derive an expression for the degeneracy in terms of the level index, $g_{tr}(\ell)$, or energy, $g_{tr}(\varepsilon)$. In Exmp. 4 we use the first, and simplest, method to derive Z_{tr}. Appendex IIIC-A demonstrates that the other two methods yield the same result and obtains expressions for g_{tr} for later reference.

Example 4. Formulate the alternative, state representation of the partition function for the high temperature limit (i.e., in analogy to eqn. IIIC-14c). Evaluate the required integrals (using Table IIIE-1) to derive an analytic expression for $Z_{tr}(T, \theta_{tr})$ valid in the limit, $T \gg \theta_{tr}$.

The series representation is a sum over the three quantum number indices. In the high-temperature limit, $T \gg \theta_{tr}$, these sums transform to a triple integral.

$$Z_{tr} = \sum_{\ell=1}^{\infty} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} e^{-(\ell^2+m^2+n^2)\theta_{tr}/T} = \int_{\ell=1}^{\infty} \int_{m=1}^{\infty} \int_{n=1}^{\infty} e^{-(\ell^2+m^2+n^2)\theta_{tr}/T} \, d\ell \, dm \, dn$$

Using the property of the exponential ($e^{a+b} = e^a e^b$), each of these integrals is separable

$$Z_{tr} = \left[\int_1^{\infty} e^{-\ell^2(\theta_{tr}/T)} d\ell \right] \cdot \left[\int_1^{\infty} e^{m^2(-\theta_{tr}/T)} dm \right] \left[\int_1^{\infty} e^{n^2(-\theta_{tr}/T)} dn \right] = \left[\int_1^{\infty} e^{\zeta^2(-\theta_{tr}/T)} d\zeta \right]^3$$

$$= \left[\int_0^{\infty} e^{\zeta^2(-\theta_{tr}/T)} d\zeta - \int_0^{1} e^{\zeta^2(-\theta_{tr}/T)} d\zeta \right]^3$$

The second of these two integrals can be expressed as an error function

$$\int_0^{1} e^{\zeta^2(-\theta_{tr}/T)} d\zeta = 2\left(\frac{T}{\pi\theta_{tr}}\right)^{\frac{1}{2}} erf\left[\left(\frac{\theta_{tr}}{T}\right)^{\frac{1}{2}}\right]$$

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[7]In Unit IIID we consider translation of subatomic particles— electrons, photons, and phonons. We will find that even the mass of an electron is sufficient that free electrons are usually within the high temperature limit for translation, $T \gg \theta_{tr,el}$.

Ans. 1. $f_{tr}(\ell,m,n) = (\ell^2 + m^2 + n^2)$, $B_{tr} = h^2/(8m^{\star}V^{2/3})$, and $\theta_{tr} = h^2/(8m^{\star}V^{2/3}k)$.

But in the limit $\lim\limits_{\varepsilon \to 0}\left[\dfrac{erf(\varepsilon)}{\varepsilon}\right]^{\frac{1}{2}} = 0$ $\qquad \left[\varepsilon = \left(\dfrac{\theta_{tr}}{T}\right) << 1\right]$

Thus only the first integral contributes. It is listed in Table IIIE-1. The result is

$$Z_{tr} = \left[\int_0^\infty e^{\zeta^2(-\theta_{tr}/T)}\, d\zeta\right]^3 = \frac{1}{8}\left(\frac{\pi T}{\theta_{tr}}\right)^{3/2}$$

The preceding problem, Exmp. 4, as well as Exer. Al of Appendix IIIC-A developed Z_{tr} in the high-temperature limit.

$$Z_{tr} = \frac{1}{8}\left(\frac{\pi T}{\theta_{tr}}\right)^{3/2}$$

Substitution of the definition of $\theta_{tr}[\equiv h^2/(8m^*v^{2/3}k)]$ gives the partition function in terms of physical parameters. To obtain preferred molar units, we simply replace the total volume with the molar volume, $V = \eta\bar{v}$. Thus,

$$Z_{tr}(T,\eta\bar{v}) = \eta\bar{v}\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2} = \eta\bar{v}\left[\frac{2\pi\bar{M}RT}{(N_A h)^2}\right]^{3/2}$$

Now that Z_{tr} has been expressed analytically the property contributions of the translational mode are determinable. A few illustrations are presented in the following problems. Results are summarized in Table IIIC-1.

Exercise 3. Apply eqns. IIIC-3 and 7 to develop expressions for the translational internal energy and constant volume specific heat.

Example 5. Apply eqn. IIIC-5 to evaluate the translational contribution to pressure in a system of independent indistinguishable particles. Examine the contribution of the internal modes to the total pressure and determine the equation of state for the gaseous system.
The translational contribution to the pressure is, eqn. IIIC-5.

$$P_{tr} = \bar{R}T\left[\frac{\partial \ln[Z_{tr}(T,\eta\bar{v})]}{\partial\bar{v}}\right]_T = \bar{R}T\frac{\partial}{\partial\bar{v}}\ln\left[\eta\bar{v}\left(\frac{2\pi\bar{M}RT}{(N_A h)^2}\right)^{3/2}\right]_T = \bar{R}T\left(\frac{\partial}{\partial\bar{v}}\ln\bar{v}\right)_T$$

Recognizing that the internal partition function, $Z_{in}(T)$, is independent of volume,

$$P = P_{tr} + \cancel{P_{in}} = \frac{\bar{R}T}{\bar{v}}$$

We find that a system of independent translating particles in the Boltzmann limit is a perfect gas.

Exercise 4. Combine the results of Exer. 3 and Exmp. 5 to deduce the translational enthalpy.

Exercise 5. . Use eqn. IIIC-11a and the results of Exer. 3 and Exmp. 5 to write an expression for the translational entropy in terms of temperature and pressure.

The solutions of the preceding problems demonstrate that once the partition function of a mode is known, the determination of its properties is relatively straightforward. In the

following sections we reinforce this general technique by applying it to other modes. Before we continue, however, we will use the present results to establish *the conditions for which the indistinguishable limit is satisfied.*

Our procedure in this unit is to apply the Boltzmann distribution to indistinguishable Bosons and Fermions. Thus the results are limited by the indistinguishable limit, $n_j^{il} = n_j^{MB}$. The limit was introduced in Sect. I as corresponding to those conditions for which no state is densely populated, $n_j \ll g_j$. Our development of Z_{tr} and its consequent equation of state, $p\bar{v} = \bar{R}T$ (or $p = n_v kT$ where $n_v = N/V = N_A/\bar{v}$), allows this vague criterion to be written explicitly in terms of the physical state of the gas. This result is developed in Appendix IIIC-A, Exmp. A1. The resulting condition is

$$\left.\frac{n_i}{g_j}\right|_{max} = n_v\left(\frac{h^2}{2\pi m^* kT}\right)^{3/2} = \frac{p}{(kT)^{5/2}}\left(\frac{h^2}{2\pi m^*}\right)^{3/2} \overset{?}{\ll} 1 \qquad (IIIC-15)$$

This relationship is the test of the indistinguishable limit. To develop a feel for the limits it imposes, consider the following illustrations.

Example 6. Nitrogen is the principal constituent in air. Does N_2 satisfy the indistinguishable limit at STP? At its normal boiling point, 77 K?

The answer to both of these queries is provided by substituting into eqn. IIIC-15. At STP

$$\left.\frac{n_i}{g_j}\right|_{max} = \frac{1.013 \cdot 10^5 N/m^2}{[1.38 \cdot 10^{-23} J/(part\ K) \cdot 300\ K]^{5/2}}$$

$$\cdot \left[\frac{(6.625 \cdot 10^{-34} Js/part)^2}{2\pi \cdot 28.01\ kg/(kg\ mol)/6.023 \cdot 10^{26} part/(kg\ mol)}\right]^{3/2} = 1.69 \cdot 10^{-7} part/state \ll 1$$

And at $T_{NBP} = 77$ K, $p = 1$ atm, $n_j/g_j|_{max} \leq 5.06 \cdot 10^{-6} part/state \ll 1$. Clearly N_2 is within the indistinguishable limit under both of these conditions.

Exmp. 6 shows that N_2 gas will not be encountered under conditions that do not satisfy the indistinguishable limit. Examining the criteria, we see that high pressure, low molecular weight, and especially low temperatures (5/2 exponent) tend to invalidate approximation IIIC-15.[8] Thus, the molecular gases that are most likely to violate the criteria are those of lowest boiling temperature.

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[8]The indistinguishable limit is separate from the independent particle, perfect gas limit. But their parametric relationship to pressure and temperature is of the same form. Thus one frequently finds that when one limit is satisfied the other is satisfied also.

Ans. 2. $V = (h^2/8m^*\theta_{tr}k)^{3/2}$. Using $\theta_{tr} = 10^{-6}K$ and $m^*_{H_2} = M_{H_2}/N_A = 3.32 \cdot 10^{-27}kg/part$, we find $V = 1.31 \cdot 10^{-18}m^3$. This corresponds to a cube whose sides are about 1 μm. To achieve higher values of θ_{tr} a smaller box would be required.

<u>Exercise 6.</u> Helium has the lowest normal boiling temperature, 4.22 K, and is therefore the most likely gas to be encountered under conditions that violate the indistinguishable limit. What is the value of $n_j/g_j|_{max}$ at its normal boiling point? If $n_j/g_j|_{max} = 10^{-2}$ part/state is accepted as a boundary of the indistinguishable limit, at what temperature would helium gas cross that boundary at atmospheric pressure?

The solution of Exer. 6 demonstrates that helium gas violates the indistinguishable limit at temperatures near its normal boiling point. The normal isotope of helium, He[4], is. a Boson. Its unique separation into two liquid phases is a result of what is called a *Bose degeneracy*, occurring when this system leaves the indistinguishable limit.

The translational (external) mode accounts for the motion of a gas molecule—our particle. We have restricted our efforts to determining its contribution to the partition function and properties, leaving detailed consideration of the distribution of particles among the translational energy levels, $\rho_{tr,j}$, for Unit IIIE. In that unit we will see that the speed distribution is a principal input to the determination of the transport properties of gases. In the following section we begin consideration of the particle's internal modes. These account for the motions of the atoms within the molecule relative to its center of gravity, as well as the motions of the electrons and nuclei within the atom relative to its center of gravity. We begin with molecular rotation.

B.   The Rotational (and Nuclear Spin) Mode

A principal internal mode is the rotation of the molecule about its center of gravity. The rotational components of a molecule can be resolved into its three principal moments of inertia, I_x, I_y and I_z. For simplicity we first consider linear molecules, $I_x = I_y \gg I_z$ (see Fig. IIIC-1). The energy levels and degeneracy for *linear rotators* are obtained from
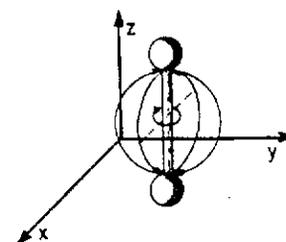
Fig. IIIC-1. Rotation of Components of a Linear Molecule

Ans. 3.	$\bar{u}_{tr} = \bar{R}T^2\left[\dfrac{\partial \ln Z_{tr}(T,n\bar{v})}{\partial T}\right]_{\bar{v}} = \bar{R}T^2\left\{\dfrac{\partial}{\partial T}\ ln\left[n\bar{v}\left(\dfrac{2\pi\bar{M}\bar{R}T}{(N_A h)^2}\right)^{3/2}\right]\right\}_{\bar{v}} = \bar{R}T^2\ \dfrac{3}{2}\left(\dfrac{1}{T}\right) = \dfrac{3}{2}\ \bar{R}T$
and	$\bar{c}_{v,tr} = \left(\dfrac{\partial \bar{u}_{tr}}{\partial T}\right)_{\bar{v}} = \dfrac{3}{2}\ \bar{R}$

Ans. 4.	$\bar{h}_{tr} = \bar{u}_{tr} + p_{tr}\bar{v} = \dfrac{3}{2}\ \bar{R}T + \left(\dfrac{\bar{R}T}{\bar{v}}\right)\bar{v} = \dfrac{5}{2}\ \bar{R}T$

Ans. 5.	$\bar{s}_{ex} = \bar{s}_{tr} = \dfrac{\bar{u}_{tr}}{T} + \bar{R}ln\left(\dfrac{Z_{tr}}{nN_A}\right) + \bar{R} = \dfrac{3}{2}\ \dfrac{\bar{R}T}{T} + \bar{R}ln\left[\left(\dfrac{kT}{p}\right)\left(\dfrac{2\pi m^* kT}{h^2}\right)^{3/2}\right] + \bar{R}$
	$= \bar{R}\left\{\dfrac{5}{2} + ln\left[\left(\dfrac{kT}{p}\right)^{5/2}\left(\dfrac{2\pi m^*}{h^2}\right)^{3/2}\right]\right\}$

a solution of the Schroedinger equation (Refs. 1, 4 or 5). In terms of its single moment of inertia ($I = I_x = I_y$; $I_z = 0$), the results, written in the form of eqn. IIIC-12, are

$$\varepsilon_{r,\ell} = B_r f_r(\ell) \qquad B_r = \frac{h^2}{8\pi^2 I} \qquad f_r(\ell) = \ell(\ell+1) \qquad g_r(\ell) = (2\ell+1) \qquad \ell = 0,1,2,3,\ldots,$$

Notice that this quantum number series, ℓ, begins with zero, and that the minimum rotational energy is zero, i.e., no rotation. Following our procedure, the rotational characteristic temperature is defined by (eqn. IIIC-13)

$$\theta_r = \frac{B_r}{k} = \frac{h^2}{8\pi^2 Ik}$$

Notice that θ_r is based on the only nonzero moment of the linear rotator. This corresponds to the principal, largest moment of linear molecules. Linear molecules include all diatomic molecules and polyatomic molecules whose atoms form a single line.

The values of θ_r for a number of diatomic and linear polyatomic molecules are listed in Table IIIC-2. All of them are much larger than the translational characteristic temperatures of the preceding section.[9] However, when we compare each substance's θ_r to its region of gaseous states, we conclude that only hydrogen and a few of the lighter hydrogen compounds have characteristic temperatures high enough that they exist in the gaseous state at temperatures on the order of θ_r. Thus, the rotational states of the vast majority of diatomic gases need only be considered in the high temperature limit, $T \gg \theta_r$. The following example develops the rotational partition function for linear rotators in this limit.

Example 7. Evaluate the rotational partition function of a rigid linear rotator in the high temperature limit, $T \gg \theta_r$.

In the high-temperature limit the partition function sum is accurately approximated by an integral

$$Z_r = \sum_{\ell=0}^{\infty} (2\ell+1)e^{-\ell(\ell+1)\theta_r/T} = \int_0^{\infty} (2\ell+1)e^{-\ell(\ell+1)\theta_r/T} \, d\ell$$

Evaluation of this integral is facilitated with the transformation, $\xi \equiv \ell(\ell+1)$, $d\xi = (2\ell+1)d\ell$, $\xi = 0$ when $\ell = 0$ and $\xi = \infty$ as $\ell \to \infty$. Thus,

$$Z_r = \int_0^{\infty} e^{-\xi\theta_r/T} \, d\xi = \frac{T}{\theta_r}$$

From Exmp. 7 the partition function and (using eqn. IIIC-10) the probability distribution for *linear rotators in the high temperature limit* are

$$Z_r = \frac{T}{\theta_r} \qquad \rho_{r,\ell} = \frac{\theta_r(2\ell+1)e^{-\ell(\ell+1)\theta_r/T}}{T}$$

[9]The fact that $\theta_r \gg \theta_{tr}$ indicates that the spacing between rotational levels is much larger than that between translational levels. By comparison, the translational energy is almost continuous.

Within the constraints imposed by the high-temperature limit, we can use these results to investigate the distribution of the particles over the rotational levels.

Exercise 7. Determine the proportion of oxygen molecules at room temperature that are in the first, second, tenth, and one hundredth rotational level.

The answer to Exer. 7 demonstrates that linear molecules are distributed broadly over the rotational levels at elevated temperatures. It also shows that there is a level of maximum occupation. This level can be determined by differentiating the rotational distribution function.

Example 8. Derive an expression for the level index of the most heavily occupied rotational level in the high temperature limit.

The level of greatest occupancy is defined by the condition, $d\rho_r(\ell)/d\ell = 0$. Then since

$$\frac{d\rho_r(\ell)}{d\ell} = \frac{d}{d\ell}\left[\frac{\theta_r}{T}(2\ell+1)e^{\ell(\ell+1)(-\theta_r/T)}\right] = \frac{\theta_r}{T}\left[2 - \frac{\theta_r}{T}(2\ell+1)^2\right]e^{\ell(\ell+1)(-\theta_r/T)}$$

Setting this derivative equal to zero and simplifying we obtain: $(-2T/\theta_r + 4\ell^2 + 4\ell + 1) = 0$. Or using the quadratic formula and eliminating the root corresponding to negative values of ℓ,

$$\ell_{max} = \left(\frac{T}{2\theta_r}\right)^{\frac{1}{2}} - \frac{1}{2}$$

Recognize that this expression will not yield an integer value for ℓ_{max}. We have used a continuous representation of ℓ. The result should be interpreted as the nearest whole number.

Exercise 8. Use the formula developed in Exmp. 8 to determine the rotational level of highest occupancy in oxygen at room temperature.

Consideration of linear rotators is simplified by the fact that they have a single appreciable moment ($I_x = I_y = I$, $I_z = 0$). Nonlinear molecules (polyatomic molecules whose atoms do not form a line) have three appreciable, potentially distinct moments. As a result nonlinear polyatomic molecules have three rotational temperatures, $\theta_{r,x}$, $\theta_{r,y}$ and $\theta_{r,z}$. (Frequently two have the same value.) The solution of the Schroedinger equation and the evaluation of the partition function series is complicated by the presence of three rotational modes. Fortunately, there are no nonlinear molecules with even a single rotational temperature large enough that its gaseous states are not within the high temperature limit $T \gg \theta_{r,x}$, $\theta_{r,y}$, $\theta_{r,z}$. Thus we need consider the *rotational partition function for nonlinear molecules* only in this limit.

Ans. 6. Following the same procedure as that of Exmp. 6, we find at the normal boiling point of helium [$p = 1.013 \cdot 10^5 N/m^2$, $T = 4.22$ K, $M = 4.003$ kg/(kg mol)] that $n_j/g_j|_{max} = 0.134$. This certainly does not satisfy the indistinguishable limit. To establish a boundary, we arbitrarily set $n_j/g_j|_{max} = 10^{-2}$ and solve for $T_{lim} = 11.9$ K. Thus helium gas at atmospheric pressure satisfies the indistinguishable limit above about 12 K.

Explain σ

$$Z_r = \frac{\pi}{\sigma} \left(\frac{T}{\hat{\theta}_r} \right)^{3/2} \qquad \text{where} \qquad \hat{\theta}_r = \left(\theta_{r,x} \cdot \theta_{r,y} \cdot \theta_{r,z} \right)^{1/3}$$

Values of $\hat{\theta}_r$ for a number of nonlinear molecules are included in Table IIIC-2.

The preceding paragraphs modeled linear molecules as rigid linear rotators ($I_x = I_y = I$, $I_z = 0$). Clearly, this is an approximation. The moment of inertia for rotation about the molecular line of centers (the z axis of Fig. IIIC-1) is not zero; it is only very small. This moment is essentially the sum of the moments of the in-line atoms for "nuclear spin." (Even though the electron orbital radii are comparatively large their mass is low enough that they do not appreciably affect the moment.) Nuclear radii are extremely small in comparison to intermolecular spacing, therefore the nuclear spin moment is many orders smaller than the molecular moment. Noting that θ_r is inversely proportional to the moment of inertia, the fact that $\theta_{ns} \sim 10^{10}$K should not be surprising. Thus, nuclear spin is not excited except at extremely high temperatures.[10]

Insofar as nuclear spin is independent of molecular rotation, the determination of the effect of spin on properties is a simple matter. But for molecules with one or more rotational symmetry axis, they are not independent. For example, consider diatomic molecule elements.

Molecular Rotation-Nuclear Spin Coupling. Diatomic molecule elements are composed of two identical atoms. Such molecules are called *homonuclear*. The identical nuclei of homonuclear diatomic molecules are indistinguishable particles within the molecule. If these nuclei have an odd number of protons and neutrons, they are Fermions (e.g., hydrogen with a single proton). If they have an even number, they are Bosons (e.g., deuterium with one proton and one neutron). It was noted briefly in Sect. IIB of Unit IIIA that Fermions have antisymmetric wave functions with respect to an exchange of identical particles and Bosons have symmetric wave functions. Further, when the ends of a diatomic molecule are exchanged, it reverses both its spin and its rotation. Thus the states of these separate modes are altered simultaneously by an exchange of identical nuclei. They are coupled and the product of the spin and rotational wave function must be even or odd depending upon the character of the nuclei. For example, if the nuclei are Fermions, then rotational states with an even wave function require a simultaneous spin state of odd wave function, and vice versa.

As explained above, rotational-nuclear spin coupling complicates the determination of the partition function and properties of the rotational-nuclear spin modes of molecules with rotational symmetry, particularly in the range, $T \sim \theta_r$. But the only symmetric molecules that are gases in this range are hydrogen and deuterium. Indeed, rotation-spin coupling is the basis of the distinction between ortho and para hydrogen. In the interest of simplicity, we forego explicit consideration of the general case (see Ref. 1, 4 or 5), but will consider only the high temperature limit of rotation-nuclear spin coupling. In this

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[10]There are instances, e.g., nuclear magnetic resonance (NMR) spectroscopy in which nuclear excitation is magnetically induced.

limit the net effect of spin on the combined partition function, $Z_{r,n}$, is division by a constant called the *symmetry number*, σ.[11] The symmetry number is equal to the number of indistinguishable molecular orientations that can be achieved through rotational transformations.

Thus, the combined rotation-nuclear spin partition function for all molecular types can be summarized in the very broad temperature range defined by $\theta_r \ll T \ll \theta_{ns}$.

Monatomic. The rare gases and most metallic vapors. In the absence of a molecular bond only nuclear spin moments are present. $\qquad Z_{r,n} = 1$

Asymmetric Linear molecules include all *heteronuclear* diatomic molecules (e.g., CO, HCl, NaCl, etc.) and linear polyatomic molecules that are not symmetric about their centers of gravity. These particles have no indistinguishable molecular orientations. Their symmetry number is one, $\sigma = 1$.[12]

$$Z_{r,n} = \frac{T}{\theta_r}$$

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[11]The results listed below are simplified by the omission of the nuclear degeneracy. In the temperature range of interest, $T \ll \theta_{ns}$, nuclear spin is unexcited and the partition function series is accurately represented by the first term. Further, the energy of the lowest nuclear (ground) level is zero. So the partition function of each nucleus is equal to its ground level degeneracy. The nuclear partition function for a molecule is $Z_{ns} = \prod_i g^o_{n,i}/\sigma$. This partition function is a constant at ordinary temperatures. It will not influence the value of any property determined by a derivative of Z. Only the magnitude of the entropy is dependent on constants in the partition function. Thus, both components of the nuclear partition function, g^o_n and σ, can be omitted in the analysis of a given substance. But if the character of the molecule is altered, σ is necessary; and if the character of the nuclei are altered, g^o_n is necessary. The results listed in the text are valid for chemical reactions but must be reformulated to include g^o_n to be valid for nuclear reactions.

[12]Since there is no rotation-nuclear spin coupling in asymmetric linear molecules, the entire range of the rotational partition function series can be employed to determine properties. Application in the range $T/\theta_r > 1$ is simplified by an approximate representation of the exponential partition function series in polynomial form.

$$Z_{r,n} = \frac{T}{\theta_r}\left[1 + \frac{1}{3}\left(\frac{\theta_r}{T}\right) + \frac{1}{15}\left(\frac{\theta_r}{T}\right)^2 + \frac{4}{315}\left(\frac{\theta_r}{T}\right)^3 + \cdots + \right]$$

Ans. 7. For oxygen at room temperature, $\theta_r/T = 2.09\ \text{K}/300\ \text{K} = 6.97 \cdot 10^{-3}$. This is certainly within the high-temperature limit. Thus, for the 1st level ($\ell = 0$)

$$\rho_r(0) = 6.97 \cdot 10^{-3} \cdot (1)e^{0 \cdot 6.97 \cdot 10^{-3}} = 0.697 \cdot 10^{-2}$$

2nd level ($\ell = 1$)

$$\rho_r(1) = 6.97 \cdot 10^{-3} \cdot (3)e^{-2 \cdot 6.97 \cdot 10^{-3}} = 2.06 \cdot 10^{-2}$$

Similarly, for the 10th level ($\ell = 9$) $\rho_r(9) = 7.07 \cdot 10^{-2}$ and the 100th level ($\ell = 99$), $\rho_r(99) = 1.49 \cdot 10^{-30}$.

Ans. 8. In oxygen at room temperature $T/\theta_r = 300\ \text{K}/2.09\ \text{K} = 144$. Thus, $\ell_{max} = (144/2)^{\frac{1}{2}} - 1/2 = 7.99$ or $\ell = 8$. This is the 9th level and its occupancy is $\rho(8) = \rho_{max} = 0.0717$.

Symmetric Linear molecules include all *homonuclear* diatomic elements and linear polyatomic molecules with a symmetry axis about their center of gravity. These particles have two indistinguishable molecular orientations, $\sigma = 2$.

$$Z_{r,n} = \frac{T}{2\theta_r}$$

Nonlinear Polyatomic molecules can have none or many symmetry axes. Each molecule must be examined as an individual case, $\sigma = ?$ (see Table IIIC-1 and the following exercise).

$$Z_{r,n} = \frac{\pi^{\frac{1}{2}}}{\sigma}\left(\frac{T}{\theta_r}\right)^{3/2}$$

Exercise 9. Identify the indistinguishable molecular orientations possible with the following molecules as sketched: Water, Methane, and Benzene.

H_2O CH_4 C_6H_6
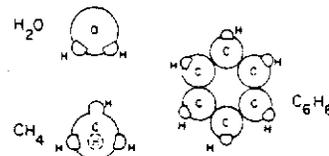
The contribution of the rotational-nuclear spin modes to the properties of each type of gaseous molecule is readily completed for each molecule type using its listed combined partition function. The required parameters, σ and θ_r, are listed in Table IIIC-2. The following problems illustrate the procedure. Complete results are given in Table IIIC-1.

Exercise 10. Determine the combined contribution of nuclear spin and molecular rotation to the properties of monatomic gases.

Example 9. Determine the combined rotation-nuclear spin contribution to the internal energy, specific heat, and entropy of a gas composed of nonlinear polyatomic molecules.

Properties are determined by application of eqns. IIIC-3 to 7. The internal energy and specific heat contributions are

$$\bar{u}_{r,n} = \bar{R}T^2 \frac{\partial}{\partial T}\left[\ln \frac{\pi^{\frac{1}{2}}}{\sigma}\left(\frac{T}{\theta_r}\right)^{3/2}\right]_{\bar{v}} = \bar{R}T^2\left(\frac{3}{2T}\right) = \frac{3}{2}\bar{R}T \qquad \bar{c}_{v,r,n} = \left(\frac{\partial u_{r,n}}{\partial T}\right)_v = \frac{3}{2}\bar{R}$$

The entropy of an internal mode is given by eqn. IIIC-11c.

$$\bar{s}_{r,n} = \frac{\bar{u}_{r,n}}{T} + \bar{R}\ln Z_{r,n} = \frac{3}{2}\bar{R} + \bar{R}\ln\left[\frac{\pi^{\frac{1}{2}}}{\sigma}\left(\frac{T}{\theta_r}\right)^{3/2}\right]$$

Exercise 11. Determine the combined rotation-nuclear spin contribution to the internal energy, specific heat, and entropy of a gas composed of symmetric linear molecules.

C.   The Vibrational Mode

The spacing between atoms in a molecule is determined by a balance of forces. Molecules are formed by ionic or covalent bonds between its atoms (see Unit ICS, Sect. I). These attractive bonds are balanced by repulsion (interference between the separate electron clouds of the atoms) if the atoms draw too close. This balance is represented for the atoms of a diatomic molecule in Fig. IIIC-2.
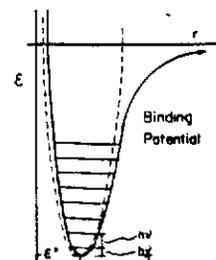
Fig. IIIC-2.
Vibrational Levels

(Note the similarity to the pair potential for molecular collisions, Unit ICS.) Near its
minimum this potential can be quite accurately approximated as a parabola. When the para-
bolic-linear spring-potential is introduced in the Schroedinger equation, the resulting
energy levels and degeneracy are

$$\varepsilon_{v,\ell} = B_v f_v(\ell) \qquad B_v = h\nu \qquad f_v(\ell) = (\ell + \tfrac{1}{2}) \qquad g_v(\ell) = 1 \qquad \ell = 0,1,2,3$$

This quantum number series, ℓ, also begins with zero, but the minimum energy is not zero,
$\varepsilon_{v,0} = h\nu/2$. Each increased energy level represents a larger amplitude (from one side of
the parabolic potential to the other) single frequency (simple harmonic) vibration of the
atoms about the mean bond distance. The vibrational energy levels are nondegenerate. The
vibrational characteristic temperature is given as

$$\theta_v = \frac{B_v}{k} = \frac{h\nu}{k}$$

Diatomic molecules are bound by a single molecular bond. Thus they have only one mode of
molecular vibration. The partition function series can be represented as an analytic
function without approximation[13]

$$Z_v = \sum_{\ell=0}^{\infty} e^{-(\ell+\frac{1}{2})\, \theta_v/T} = e^{-\theta_v/2T} \sum_{\ell=0}^{\infty} \left(e^{-\theta_v/T} \right)^{\ell} = \frac{e^{-\theta_v/2T}}{1 - e^{-\theta_v/T}}$$

Since Z_v is represented as an analytic function, the vibration mode distribution can be
determined in general. That is, without recourse to low or high temperature approxima-
tions. This is fortunate since vibration characteristic temperatures range from below
normal to moderately high temperatures. Therefore, one commonly requires vibrational
properties near the various characteristic temperatures. The probability distribution for
a vibrational mode is

$$\rho_v(\ell) = \left(1 - e^{-\theta_v/T} \right) \left(e^{-\theta_v/T} \right)^{\ell}$$

Exercise 12. Determine the percentage of particles that are in the 1st, 2nd, and 10th
vibrational level at the following temperatures: $T = 0.1\,\theta_v$, θ_v, and $10\,\theta_v$.

The results of Exer. 12 show that the population in the vibrational levels shifts from the
lowest toward higher levels as the temperature increases with respect to θ_v.

The contribution of the vibrational mode to the properties of a diatomic gas is de-
terminable from Z_v and its derivatives. Results are listed in Table IIIC-1 and illus-
trated in the following exercise.

Exercise 13. Derive expressions for $\bar{u}_v$, $\bar{c}_{v,v}$, and $\bar{s}_v$ for a diatomic gas.

---

[13]The infinite series is of the form

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \qquad |x| \leq 1$$

A diatomic molecule is formed by a single molecular bond; it has one mode of inter-molecular vibration. A polyatomic molecule has at least two bonds. The number of modes of molecular vibration exhibited by a polyatomic molecule can be determined as follows.

> Modes of Molecular Vibration. Consider each atom within a molecule to be a separate mass point. A mass point has three independent directions of motion—*three degrees of freedom*. Thus, the total number of degrees of freedom associated with the n_a atoms composing a molecule is $3n_a$. The translation of the molecule accounts for the three possible directions of motion of the center of gravity of the molecule. This comprises three degrees of freedom. The rotational mode models rigid body rotation of the atoms about the particle's center of gravity. For linear molecules rotation in the two planes of nonzero moment uses two degrees of freedom. For nonlinear molecules the three planes of rotation use three degrees of freedom. All remaining degrees of freedom of the n_a atoms must be accounted for in intermolecular distortions. Thus, the number of modes of molecular vibration in *Linear and Nonlinear Molecules* respectively, are
>
> $$P_\ell = 3n_a - 5 \qquad P_{n\ell} = 3n_a - 6 \qquad \text{(IIIC-16a,b)}$$

Exercise 14. How many vibrational modes are present in the linear molecule CO_2 and the nonlinear molecules H_2O, NH_3 and C_6H_6?

The natural frequency of each vibrational mode, ν_p, defines its individual characteristic temperature, $\theta_{v,p}$ ($\equiv h\nu_p/k$). (Modes with the same characteristic temperature are common.) At temperatures not more than an order above the lowest value of $\theta_{v,p}$ these

Ans. 9. There are two indistinguishable orientations of a water molecule, as shown. Thus the symmetry number for water is $\sigma = 2$.
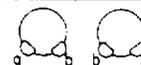
Methane can be rotated through three indistinguishable positions with any of the four hydrogen molecules on the axis of rotation. This must be repeated with each of the four hydrogen atoms on the axis of rotation, thus $\sigma = 3 \cdot 4 = 12$.
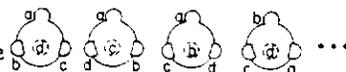
The hexagonal benzene molecule can be rotated through six indistinguishable positions. Then the molecule can be rotated on a vertical axis to give a new indistinguishable orientation. In this new orientation the previous six horizontal rotations can be repeated. Thus, $\sigma = 6 \cdot 2 = 12$.
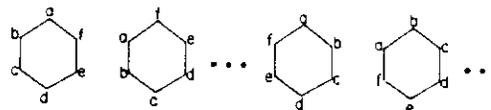
Ans. 10. For monatomic gas $Z_{r,n} = 1$. Then $\ln Z_{r,n} = \ln 1 = 0$. Thus, spin-rotation does not contribute to the properties of monatomic gases in the temperature range $T \ll \theta_n$. [A more complete treatment would be $Z_{r,n} = g_n^o$ (= 2 for monatomic gases), see footnote 11. Thus there is a constant contribution to entropy and functions of entropy, but none to other properties.]

Ans. 11.

$$\bar{u}_{r,n} = \bar{R}T^2\left[\left(\frac{\partial}{\partial T}\right)\ln\left(\frac{T}{2\theta_r}\right)\right]_{\bar{v}} = \bar{R}T \quad \text{and} \quad c_{v(r,n)} = \left(\frac{\partial \bar{u}_{r,n}}{\partial T}\right)_{\bar{v}} = \bar{R}$$

$$\bar{s}_{r,n} = \frac{\bar{u}_{r,n}}{T} + \bar{R}\ln Z_{r,n} = \bar{R} + \bar{R}\ln\left(\frac{T}{2\theta_r}\right)$$

modes can be considered independent simple harmonic oscillators.[14] When this is the case, each vibrational mode has its own partition function and

$$Z_v = \prod_{p=1}^{P} Z_{v,p} = \prod_{p=1}^{P} \frac{e^{-\theta_{v,p}/2T}}{\left(1 - e^{-\theta_{v,p}/T}\right)}$$

Values of $\theta_{v,p}$ for a number of polyatomic gases are listed in Table IIIC-2.[15] These data permit the determination of the vibrational contribution to the properties of polyatomic gases. Since the total vibrational partition function is the product of the separate mode partition functions, the total vibrational properties are the sum of the contribution of the separate modes. Thus, the results of Exer. 13 can be applied to each mode separately, see Table IIIC-1.

---

[14]As the amplitude of vibration increases several factors combine to distort the assumption of the independent, simple harmonic vibrational model. The potential well is not parabolic at higher energy levels, Fig. IIIC-2. Coupling between vibrational modes will occur and at high vibrational amplitudes the oscillation in molecular moment will cause rotation vibration coupling.

[15]The number of modes of a given frequency are designated by their number in parentheses, $\theta_{v,p}(2)$, etc., in Table IIIC-2.

Ans. 12. The levels of interest are the 1st ($\ell = 0$), the 2nd ($\ell = 1$) and the 10th ($\ell = 9$). At $T = 0.1\,\theta_v$

$$\rho_v(0) = (1 - e^{-10})(e^{-10})^0 = 0.99995, \quad \rho_v(1) = (1 - e^{-10})(e^{-10})^1 = 4.54 \cdot 10^{-5}$$

and

$$\rho_v(9) = 8.19 \cdot 10^{-40}.$$

Similarly, at $T = \theta_v$: $\rho_v(0) = 0.632$, $\rho_v(1) = 0.233$, $\rho_v(9) = 2.87 \cdot 10^{-5}$

and at $T = 10\,\theta_v$: $\rho_v(0) = 0.0861$, $\rho_v(1) = 0.0779$, $\rho_v(9) = 0.0387$

Ans. 13.

$$\bar{u}_v = \bar{R}T^2 \left\{ \frac{\partial}{\partial T} \ln \left[\frac{e^{-\theta_v/2T}}{\left(1 - e^{-\theta_v/T}\right)} \right] \right\}_{\bar{v}} = \bar{R}T^2 \frac{d}{dT} \left[-\frac{\theta_v}{2T} - \ln\left(1 - e^{-\theta_v/T}\right) \right]$$

$$= \bar{R}T^2 \left[+\frac{\theta_v}{2T^2} - \frac{-(\theta_v/T^2)e^{-\theta_v/T}}{\left(1 - e^{-\theta_v/T}\right)} \right] = \bar{R}\,\theta_v \left[\frac{1}{2} + \frac{1}{\left(e^{\theta_v/T} - 1\right)} \right]$$

$$\bar{c}_{v,v} = \left(\frac{\partial \bar{u}_v}{\partial T} \right)_v = \frac{\partial}{\partial T} \left\{ \bar{R}\,\theta_v \left[\frac{1}{2} + \frac{1}{\left(e^{\theta_v/T} - 1\right)} \right] \right\}_{\bar{v}} = \bar{R}\theta_v \left[\frac{(\theta_v/T^2)e^{\theta_v/T}}{\left(e^{\theta_v/T} - 1\right)^2} \right] = \frac{\bar{R}(\theta_v/T)^2\, e^{\theta_v/T}}{\left(e^{\theta_v/T} - 1\right)^2}$$

$$\bar{s}_v = \frac{\bar{u}_v}{T} + R\ln Z_v = \bar{R}\left(\frac{\theta_v}{T}\right)\left[\frac{1}{2} + \frac{1}{\left(e^{\theta_v/T} - 1\right)} \right] + \bar{R}\ln\left[\frac{e^{-\theta_v/2T}}{\left(1 - e^{-\theta_v/T}\right)} \right] = \bar{R}\left[\left(\frac{\theta_v}{T}\right)\frac{1}{\left(e^{\theta_v/T} - 1\right)} - \ln\left(1 - e^{-\theta_v/T}\right) \right]$$

Of all the modes to be considered, only vibration is
commonly encountered near its characteristic temperature
$(T \sim \theta_v)$. In fact, for polyatomic gases it is uncommon
for at least one vibrational mode not to be in such a re-
gion. In addition, vibration is the first mode whose prop-
erties can be analytically determined at all temperatures.
(Translational and rotational consideration was limited to
high temperatures, and nuclear spin to low temperatures.)
A more thorough study of these modes would reveal that the
general behaviors of all internal modes are very similar.
Thus, a study of the relationship between the low, high, and


Fig. IIIC-3. Vibrational
Specific Heat

intermediate temperature properties of a vibrational mode will improve our perception of
properties in general. Fig. IIIC-3 presents a graphical representation of the $c_{v(v,p)}$ as
a function of dimensionless vibrational temperature, T/θ_v. (The function plotted appears
in Table IIIC-1 and Ans. 13.) At low temperatures $c_{v,v} \Rightarrow 0$. As $T \Rightarrow \theta_v$, $c_{v,v}$ increases
sharply approaching the limit $2(\bar{R}/2)$ as $T \gg \theta_v$. Except for the multiple of $(\bar{R}/2)$ in the
high-temperature limit, these are general characteristics of all modes. We summarize:

Low-Temperature Limit, $T \ll \theta$. In this limit a mode is said to be unexcited.
Its particles condense into the lowest accessible levels.[16] An internal mode's
particles condense into the lowest "ground" level, $\rho_{p,1} \Rightarrow 1$. Thus, the spac-
ing between the first and second level is very important to the distribution.
This is the quantum limit. Such modes contribute no more than a constant to
properties. The constant is zero for the specific heat.

High-Temperature Limit, $T \gg \theta$. In this limit a mode is said to be fully excited.
The particles are distributed broadly over many levels. The spacing between
levels is negligible in comparison to the average energy of the particles.
Thus, energy can be considered continuous. This is the Newtonian or classical
limit of the mode. The energy contribution of modes is a constant multiple of
$\bar{R}T/2$ and its specific heat contribution is a constant multiple of $\bar{R}/2$.[17]

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[16]The low-temperature limit of the external (translational) mode is complicated by
the consequences of particle symmetry. Bosons condense into the lowest level in a manner
similar to that discussed above. But Fermions are limited to no more than a single par-
ticle per state. Thus they will crowd into the lowest available empty states. The dis-
tinction between these two distinct low-temperature "degenerate" conditions causes their
low-temperature behavior to be quite different. Unit IIID treats free electron behavior
in metals. This is an illustration of degenerate Fermion behavior.

[17]The fact that the classical limit contribution to the energy is a multiple of
$kT/2 (k \equiv \bar{R}/N_A)$ per particle is called the *equipartition of energy* principle. It requires
that the discrete energy spectrum approach a continuum (the high temperature limit) and
that the energy be expressible in a quadratic form (Ref. 4, pg. 72). These characteris-
tics are shared by the translational, rotational, and vibrational modes.

Ans. 14. $P_{\ell,CO_2} = 3 \cdot 3 - 5 = 4,$ $P_{n\ell,H_2O} = 3 \cdot 3 - 6 = 3,$ $P_{n\ell, NH_3} = 3 \cdot 4 - 6 = 6,$
$P_{n\ell,C_6H_6} = 3 \cdot 12 - 6 = 30.$

From the preceding discussion, it should be clear that one cannot talk about high or low temperatures without qualifying which mode or modes are meant.

Exercise 15. Verify the low and high temperature asymptotes represented in Fig. IIIC-3 by applying the corresponding limits to the vibrational specific heat function (see Exer. 13).

$$\bar{c}_{v,v} = \bar{R}\left(\frac{\theta_v}{T}\right)^2 \frac{e^{\theta_v/T}}{\left(e^{\theta_v/T}-1\right)^2}$$

Hint: Use the fact that $e^x \Rightarrow \infty$ as $x \Rightarrow \infty$ and $e^x = 1 + x$ as $x \Rightarrow 0$.

D. Electronic (Dissociation) Mode

The bound electrons of an atom are tied to its nucleus by coulombic attraction. For a *single electron (hydrogen) atom* the Schroedinger equation can be solved to obtain the electronic energy levels and their degeneracy.

$$\varepsilon_{el,H}(\ell) = B_{el,H}f_{el}(\ell) \qquad B_{el,H} = \frac{e^4 m_e^*}{8\varepsilon_o^2 h^2} \qquad f_{el,H}(\ell) = -\frac{1}{\ell^2} \qquad g_{el,H}(\ell) = 2\ell^2 \qquad \ell = 1,2,3,..,$$

in which θ is the charge, m_e^* is the rest mass of the elctron, and ε_o is the permittivity of free space. Notice that the minimum, ground level, energy is negative. Work must be done to remove the electron from the atom. That is, energy must be added to ionize the atom. The electronic characteristic temperature of a hydrogen atom is

$$\theta_{el,H} = \frac{B_{el,H}}{k} = \frac{e^4 m_e^*}{8\varepsilon_o^2 h^2 k}$$

Exercise 16. Determine the magnitude of the electronic characteristic temperature of a hydrogen atom.

The solution of Exer. 16 shows that $\theta_{el,H} \sim 10^5 K$. Thus even at combustion level temperatures, a hydrogen atom's electronic mode is unexcited. It would contribute no more than a constant to properties, and nothing to property changes.

A solution of the Schroedinger equation for a multielectron atom requires that repulsion between the like charge electrons be accounted for in addition to their attraction to the nucleus. This problem is as yet too difficult for exact analytic solution. Analysis of a molecule is even more difficult, as the electrons are then repelled by one another and attracted to all of the nuclei, simultaneously. Thus neither the level series nor θ_{el} can be analytically determined for particles that are more complex than the one electron atom, viz., the hydrogen atom. Instead these parameters are inferred from spectroscopic measurement.[18] A study of these data shows that the magnitude determined for a

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[18]Since the magnitudes of θ_{el} are quite high, only the first few levels are needed. The parameters required for the rotational and vibrational modes are also obtained spectroscopically θ_r, $\theta_{v,p}$. But since the model is valid only a single parameter is needed.

hydrogen atom, Exer. 16, is representative of all atoms and molecules, $\theta_{el} \sim 10^5$K. Thus we can determine the properties of given independent indistinguishable atoms or molecules at ordinary temperatures without regard to the electronic mode.

As the temperature of a gas increases,its electronic mode begins to be excited. Electronic excitation affects the properties of the substance in a manner that is similar to other modes. However, electrons that are sufficiently excited will *dissociate* from the particle creating a *plasma*— a mixture of free electrons and positive ions. This radically changes the electric properties of the gas; it becomes conducting. Thus the electronic mode is significant at somewhat lower excitation levels than other modes. Finally, when particles are altered as a result of a chemical reaction, atoms are shifted from one type of particle to another. This requires dissociation of atoms from the participating molecules. The energy of molecular dissociation is normally reported in terms of electronic energy levels. Thus the change in the electronic partition function is a principal term in the evaluation of the effects of chemical reactions even when the electronic modes of the reactants and their products are unexcited preceding and following the reaction. The use of the electronic mode in the study of ionization and chemical reactions is considered briefly in Appendix IIIC-B.

This concludes the development of the unit. The following section summarizes the contributions of translational, rotation-nuclear spin, and vibrational modes for given particles.

IV. PROPERTIES OF MOLECULAR PERFECT GASES

The preceding sections considered external translation and each internal mode of a molecular gas. We found that property changes that occur to a given substance can be determined considering only its translational, rotational-nuclear spin, and vibrational modes. The necessary data (θ_r, σ and $\theta_{v,p}$) are provided in Table IIIC-2. Analytic expressions for each of the required partition functions Z_{tr}, $Z_{r,n}$ and $Z_{v,p}$ were developed, and the procedures by which their corresponding properties are determined were illustrated by example and exercise. Complete results are summarized in Table IIIC-1. The objective of this section is to combine the effects of the separate modes to determine overall properties. Since our eventual interest lies in property changes we choose to ignore the constants introduced by the electronic, see Appendix IIIC-B, and nuclear binding mode; and we will, therefore, refer to the sum of the translational, rotational-nuclear spin, and vibrational modes as though they were total properties.

Example 10 Write an expression for the partition function, internal energy, enthalpy, specific heats,and entropy of a system of independent, nonlocalized atoms.
We extract the necessary expression for Z, $\bar{u}^*$, $\bar{c}_v^*$, and $\bar{s}^*$ from Table IIIC-1.

$$Z = Z_{tr} Z_{r,n} Z_v = n\bar{v}\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2} \cdot 1 \cdot 1 \qquad \bar{u}^* = \frac{3}{2}\bar{R}T + 0 + 0$$

$$\bar{c}_v^* = \frac{3}{2}\,\bar{R} + 0 + 0 = \frac{3}{2}\,\bar{R} \qquad \bar{s}^* = \bar{R}\left\{\frac{5}{2} + \ell n\left[\frac{(kT)^{5/2}}{p}\left(\frac{2\pi m^*}{h}\right)^{3/2}\right]\right\}$$

The enthalpy and specific heat at constant pressure are

$$\bar{h}^* = \bar{u}^* + \bar{R}T = \frac{5}{2}\,\bar{R}T \qquad \bar{c}_p^* = \bar{c}_v^* + \bar{R} = \frac{5}{2}\,\bar{R}$$

Exercise 17. Use the functions of Table IIIC-1 and the values of Table IIIC-2 to determine c_p for nitrogen at atmospheric pressure at the temperature levels 50, 300, 600, 1500, 3500, and 5000 K. Compare the results to the recommended "near room temperature" value, Table ID-1. Draw conclusions with respect to the effectiveness of the calculation and the contribution of each mode.

The results of Exmp. 10 and Exer. 17 demonstrate the meaning and limitation of the "near room temperature" specific heat values recommended for monatomic and diatomic gases, see Table ID-1. The recommendation for monatomic gases $[\bar{c}_v^* = (3/2) \cdot \bar{R}, \bar{c}_p^* = (5/2) \cdot \bar{R}$, and $\gamma^* = 1.67]$ is simply the translational contribution. Since there is no molecular rotation or vibration in monatomic gases this approximation is valid for perfect gas states until the electronic mode is initiated, $T \sim 10^4 K$. The recommendation for diatomic gases $[\bar{c}_v^* = (5/2) \cdot \bar{R}, \bar{c}_p^* = (7/2) \cdot \bar{R}, \gamma^* = 1.4]$ is the sum of the translational and fully excited rotational mode contributions. All diatomic molecules except hydrogen and deuterium have fully excited rotational modes at all achievable gaseous states. (Even these exceptions occur only at their lowest gaseous temperatures.) Thus in practice "near room temperature" means from the lowest gaseous temperatures until the vibrational mode is energized, viz., at temperatures above $T \sim \theta_v/8$.

Exercise 18. Determine $\bar{c}_p^*$ for methane at 200, 400, 800, 1600, and 3200 K.

Ans. 15. In the low-temperature limit, $\theta_v/T \Rightarrow \infty$ and $\exp(\theta_v/T) - 1 \Rightarrow \exp(\theta_v/T)$

$$\bar{c}_{v,v} \Rightarrow \bar{R}\left(\frac{\theta_v}{T}\right)^2 e^{-\theta_v/T} \Rightarrow 0$$

In the high-temperature limit, $\theta_v/T \Rightarrow 0$ and $\exp(\theta_v/T) \Rightarrow 1 + (\theta_v/T)$. So

$$\bar{c}_{v,v} = \bar{R}\left(\frac{\theta_v}{T}\right)^2 \frac{[1 + (\theta_v/T)]}{[1 + (\theta_v/T) - 1]^2} \Rightarrow \bar{R}$$

Ans. 16. The required constants are listed in Table IA-2.

$k = 1.380 \cdot 10^{-23} J/(part\ K), \qquad h = 6.625 \cdot 10^{-34} Js/part, \qquad e = 1.602 \cdot 10^{-19} C/part,$

$m_e^* = 9.109 \cdot 10^{-28} g/part, \qquad \varepsilon_o = 8.854 \cdot 10^{-12} C/(Vm)$

$$\theta_{el,H} = \frac{1.602^4 \cdot 10^{-76} C^4 \cdot 9.109 \cdot 10^{-31} kg \cdot (1\ J/Cv)^2}{8 \cdot (8.854)^2 \cdot 10^{-24} C^2/(Vm)^2 \cdot (6.625)^2 \cdot 10^{-68} (J\ s)^2 \cdot 1.380 \cdot 10^{-23} J/K}$$

$$= 1.579 \cdot 10^5 K$$

Exer. 18 shows that the specific heat of gaseous methane varies at all temperature levels. Its lowest vibrational excitation is initiated below normal temperatures and one or more vibrational modes contribute variably as the temperature increases. This is representative of all polyatomic molecules. So the assumption of constant specific heats is a poor approximation for the analysis of polyatomic gas molecules.

It might be noted that both Exers. 17 and 18 require that $\bar{c}_p^{-*}$ be evaluated at temperatures at which their respective species are not perfect gases at atmospheric pressure. Even though the substance is not within the perfect gas region its perfect gas properties can be calculated. We will find that the general method of determining imperfect gas and condensed phase properties, Units IVD and IVF, is based on their deviation from a perfect gas reference value. Thus a prediction of perfect gas properties at all temperature levels is an essential step in property determination. The methods developed in this unit have been employed to compile an exhaustive collection of perfect gas properties, the JANAF Tables.[19] Exers. 17 and 18 have shown how the $\bar{c}_p^{-*}$ data is computed. The following problems demonstrate the compilation of enthalpy and entropy.

Example 11. Write expressions for the enthalpy and entropy change of carbon dioxide. Determine the values of these changes from 298 to 500, 1000, and 3000 K at atmospheric pressure.

Carbon dioxide is a linear polyatomic molecule. Its enthalpy is given by (see Table IIIC-1).

$$\bar{h}^*(T) = \bar{u}_{tr}^*(T) + \bar{u}_{r,n}^*(T) + \bar{u}_v^*(T) + \bar{R}T = \bar{R}\left\{\frac{7}{2}T + \sum_{p=1}^{4}\theta_{v,p}\left[\frac{1}{2} + \frac{1}{\left(e^{\theta_{v,p}/T_o} - 1\right)}\right]\right\}$$

Thus, the enthalpy change is

$$\bar{h}^*(T) - \bar{h}^*(T_o = 298\ K) = \bar{R}\left\{\frac{7}{2}(T - T_o) + \sum_{p=1}^{4}\theta_{v,p}\left[\frac{1}{\left(e^{\theta_{v,p}/T} - 1\right)} - \frac{1}{\left(e^{\theta_{v,p}/T_o} - 1\right)}\right]\right\}$$

The entropy and entropy change are written in an analogous manner. We write only the entropy change, thus eliminating the constants and pressure dependent terms.

$$\bar{s}^*(T, 1\ atm) - \bar{s}^*(T_o, 1\ atm) = \bar{R}\left\{\frac{7}{2}\ln(T/T_o) + \sum_{p=1}^{4}\theta_{v,p}\left[\frac{1}{T\left(e^{\theta_{v,p}/T} - 1\right)}\right.\right.$$

$$\left. - \frac{1}{T_o\left(e^{\theta_{v,p}/T_o} - 1\right)}\right] - \ln\left(\frac{1 - e^{-\theta_{v,p}/T}}{1 - e^{-\theta_{v,p}/T_o}}\right)\Big\}$$

Table IIIC-2 gives the necessary vibrational temperatures: 960.1 K (2), 1932 K, 3380 K. Thus we find

T(K)	$\dfrac{\bar{h}^*(T) - \bar{h}^*(T_o)}{\bar{R}}$	(K)	$\dfrac{\bar{s}^*(T, 1\ atm) - \bar{s}^*(T_o, 1\ atm)}{\bar{R}}$
500	999.4		2.540
1000	3939		6.598
3000	18220		14.398

Exercise 19. Determine the enthalpy and entropy change when carbon monoxide is heated at atmospheric pressure from 298 to 1000 K. (Answer on pg. 28.)

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[19]The JANAF Tables include the electronic mode, coupling between the rotational and vibrational modes, and other effects which allow greater accuracy.

It should be noted that the determination of these property changes were independent of both the symmetry number and the rotational characteristic temperature, σ and θ_r. A determination of the absolute entropy requires these parameters. The JANAF Tables tabulate absolute entropy, but the tabulated enthalpy is relative. Hence the constants employed are different from those of the above formulations.[20] In other respects the results of this section are compatible with the JANAF compilation.

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[20]The entropies of the JANAF Table are referenced to absolute zero temperature. The tables permit a determination of absolute enthalpy using the enthalpy of formation of each molecule from its constituent elements. This determination is dependent on the electronic-dissociation mode, see Appendix IIIC-B.

Ans. 17. Nitrogen is a homonuclear diatomic element, hence

$$\bar{c}_p^* = \bar{c}_{v,tr}^* + \bar{c}_{v(r,n)}^* + \bar{c}_{v,v}^* + \bar{R} = \bar{R}\left[\frac{3}{2} + 1 + \left(\frac{\theta_v}{T}\right)^2 \frac{e^{\theta_v/T}}{\left(e^{\theta_v/T} - 1\right)^2} + 1\right]$$

For nitrogen $\theta_v = 3392$ K. Then substituting we obtain
The normal boiling point of nitrogen is 77 K. Thus at 50 K atmospheric nitrogen is condensed and $\bar{c}_p^*$ is not appropriate. Up to 600 K the vibrational mode is unexcited, $\bar{c}_p^* \approx (7/2)\,\bar{R}$, the "near room temperature value." At 5000 K the vibrational mode is almost fully excited ($\bar{c}_p^* \Rightarrow 9/2\,\bar{R}$); but at this level electronic excitation is beginning and cannot be overlooked.

T(K)	50	300	600	1500	3500	5000
$\frac{\bar{c}_p^*}{\bar{R}}$	3.50	3.502	3.613	4.164	4.425	4.563

Ans. 18. Methane, CH_4, is a nonlinear molecule with 5 atoms. It has 9 vibrational modes. Hence

$$\bar{c}_p^* = \bar{c}_v^* + \bar{R} = \bar{R}\left[\frac{3}{2} + \frac{3}{2} + \sum_{p=1}^{9} \left(\frac{\theta_{v,p}}{T}\right)^2 \frac{e^{\theta_{v,p}/T}}{\left(e^{\theta_{v,p}/T} - 1\right)^2} + 1\right]$$

Fortunately there are only four distinct values of $\theta_{v,p}$: 1879 K (3), 2207 (2), 4196 K, and 4343 K (3). Thus,

T(K)	200	400	800	1600	3200
$\frac{\bar{c}_p^*}{\bar{R}}$	4.026	4.371	7.569	10.65	12.29

Ans. 19. Carbon monoxide is heteronuclear diatomic. Thus, its enthalpy and entropy change are

$$\bar{h}^*(T) - \bar{h}^*(T_o) = \bar{R}\left\{\frac{7}{2}(T-T_o) + \theta_v\left[\frac{1}{\left(e^{\theta_v/T} - 1\right)} - \frac{1}{\left(e^{\theta_v/T_o} - 1\right)}\right]\right\}$$

$$\bar{s}^*(T, 1\,atm) - \bar{s}^*(T_o, 1\,atm) = \bar{R}\left\{\frac{7}{2}\ln\left(\frac{T}{T_o}\right) + \theta_v\left[\frac{1}{T}\frac{1}{\left(e^{\theta_v/T} - 1\right)} - \frac{1}{T_o}\frac{1}{\left(e^{\theta_v/T_o} - 1\right)}\right] - \ln\left(\frac{1-e^{-\theta_v/T}}{1-e^{-\theta_v/T_o}}\right)\right\}$$

Then substituting $\theta_v = 3121$ K, we obtain $[\bar{h}^*(1000\text{ K}) - \bar{h}^*(298\text{ K})]/\bar{R} = 2601$ K, $[\bar{s}^*(1000\text{ K}, 1\text{ atm}) - \bar{s}^*(298\text{ K}, 1\text{ atm})]/\bar{R} = 4.336$.

FURTHER CONSIDERATION OF THE TRANSLATION MODE

Exmp. 4 develops Z_{tr} using the states formulation. This is the easiest and therefore the preferred method. But developments to be completed in Units IIID and IIIE require formulation of particle distribution over translational levels. Specifically, an analytic expression for the degeneracy, g_{tr}, is required. The following example uses the result of Exmp. 3 to deduce this function.

Example Al. Exmp. 4 formulated Z_{tr} in the limit $T \gg \theta_{tr}$ as a triple integral over the quantum numbers. In a geometric sense the quantum numbers were the coordinates of a cartesian spatial description of the states and the integration was over the positive quadrant. The magnitude of an energy state, $\varepsilon(\ell,m,n)$, is proportional to the square of its position vector $(\ell^2 + m^2 + n^2)$. Thus states of the same energy are connected by spherical surfaces within the positive quadrant $(\ell,m,n > 0)$. The level index, q, is proportional to the magnitude of the energy. And the number of states per level is proportional to the area of the spherical segment. Thus $q^2 = \ell^2 + m^2 + n^2$ provides a direct analogy between the two representations. Derive an analytic expression for the degeneracy, $g_{tr}(q)$, using this analogy by transforming the cartesian states integral to a spherical level integral.

The triple integral over the states developed in Exmp. 4 is to be transformed under the definition $\ell^2 + m^2 + n^2 = q^2$. Thus the element of volume in the cartesion space transforms to $d\ell \, dm \, dn = q^2 \cos\theta \, d\theta \, d\phi \, dq$. And while $1 \le n,m,\ell < \infty$ the new coordinates satisfy the limits: $0 \le \theta \le \pi/2$, $0 \le \phi \le \pi/2$, $\sqrt{3} \le q < \infty$. Thus

$$Z_{tr} = \left(\int_1^\infty e^{-\ell^2 \theta_{tr}/T} \, d\ell \right) \left(\int_1^\infty e^{-m^2 \theta_{tr}/T} \, dm \right) \left(\int_1^\infty e^{-n^2 \theta_{tr}/T} \, dn \right)$$

$$= \int_0^{\pi/2} \cos\theta \, d\theta \int_0^{\pi/2} d\phi \int_{\sqrt{3}}^\infty e^{-q^2 \theta_{tr}/T} q^2 dq = \frac{\pi}{2} \int_{\sqrt{3}}^\infty q^2 e^{-q^2 \theta_{tr}/T} \, dq$$

Comparing this result to eqn. IIIC-14c, we conclude, $g_{tr}(q) = \pi q^2/2$.

Exercise Al. Exmp. Al formulated Z_{tr} for the limit $T \gg \theta_{tr}$ in terms of an integral over the levels. Verify that this result is correct by completing the required integral (use Table IIIE-1) and comparing the result to that of Exmp. 4.

Exmp. 4 and Exer. Al formulated the high-temperature limit translational partition function in two of its three possible integral forms, viz., as an integral over the states and levels. The third formulation is as an integral over the energy magnitudes themselves.

Exercise A2. Transform the level integral formulation of Exmp. 1 to an integral over the energy. Identify the degeneracy, $g_{tr}(\varepsilon)$.

Exer. A2 expressed $g_{tr}(\varepsilon)$ in terms of θ_{tr}. In Unit IIID, we will employ this function to determine the equilibrium properties of electromagnetic and acoustical radiation, and

free electrons. Therefore, we set out the result in terms of the particle's parameters.

$$g_{tr}(\varepsilon) = \frac{\pi}{4} \frac{\varepsilon^{1/2}}{(k\,\theta_{tr})^{3/2}} = 4\pi V \left(\frac{2m^*}{h^2}\right)^{3/2} \varepsilon^{1/2} \qquad \text{(IIIC-A1)}$$

This unit is devoted to the determination of the properties of indistinguishable particles in their Boltzmann limit. Therefore, it would be imprudent to apply these methods without testing to see that the limit, $n_j \ll g_j$, is satisfied.

Exercise A3. Show that the states of the first (or ground) level have the highest occupancy.

Exer. A3 shows that it is not necessary to investigate the entire level index series, since $n_j/g_j|_{max} = n_1/g_1$. A further simplification can be achieved when we recognize that the values of θ_{tr} (see Sect. IIIA) are many orders of magnitude smaller than the value of any individual characteristic temperature of an internal mode, $\theta_p \gg \theta_{tr}$ (see Sects. IIIB, C, and D). Therefore, the translational mode is excited at far lower temperatures than any of the internal modes. In the following example we exploit this fact to reduce the indistinguishable limit test to a function of the translational mode alone.

Example A2. Under the assumption that the translational mode is fully excited, $T \gg \theta_{tr}$, study the effect of the internal modes on the prediction of n_1/g_1.

We can write for the separate translational and internal modes: $g_1 = g_{tr,1}g_{in,1}$, $\varepsilon_1 = \varepsilon_{tr,1} + \varepsilon_{in,1}$, and $Z = Z_{tr}Z_{in}$. Then assuming that the limit is satisfied, we can write

$$\frac{n_1}{g_1} = \frac{N\,e^{-\varepsilon_1/kT}}{Z} = N\left(\frac{e^{-\varepsilon_{tr,1}/kT}}{Z_{tr}}\right)\left(\frac{e^{-\varepsilon_{in,1}/kT}}{Z_{in}}\right)$$

Consider an expansion of the reciprocal of the internal mode term.

$$\left(\frac{Z_{in}}{e^{-\varepsilon_{in,1}/kT}}\right) = \left[\left(g_1\,e^{-\varepsilon_1/kT} + g_2\,e^{-\varepsilon_2/kT} + g_3\,e^{-\varepsilon_3/kT} + \cdot+\right)e^{\varepsilon_1/kT}\right]_{in}$$
$$= g_1 + g_2\,e^{-(\varepsilon_2-\varepsilon_1)/kT} + g_3\,e^{-(\varepsilon_3-\varepsilon_1)/kT}$$

Then when we recognize that the internal mode is, at least, much less excited than translational mode, we expect $(Z\,e^{\varepsilon_1/kT})_{in} \approx g_{in,1}$. Thus

$$\frac{n_1}{g_1} = \frac{n_1}{g_{tr,1}\,g_{in,1}} \leq \frac{N\,e^{-\varepsilon_{tr,1}/kT}}{Z_{tr}\,g_{in,1}}$$

Finally, the translational mode is assumed to be fully excited; so $T \gg \theta_{tr} = (\varepsilon_{tr,1}/3k)$. Thus the limit test simplifies to

$$\frac{n_{tr,1}}{g_{tr,1}} \leq \frac{N}{Z_{tr}} \ll 1$$

Exmp. A2 reduced the limit test to a function of translational mode parameters alone, $n/Z_{tr} \ll 1$. When we use the expression for Z_{tr}

$$Z_{tr} = \bar{v}\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2}$$

and its consequent equation of state (see Exmp. 5) $p\bar{v} = \bar{R}T$ or $p = n_v kT$ where n_v is the particle number density $(n_v \equiv N/V = N_A/\bar{v})$, we obtain

$$\left.\frac{n_j}{g_j}\right|_{max} \simeq \frac{N}{Z_{tr}} = n_v\left(\frac{h^2}{2\pi m^* kT}\right)^{3/2} = \frac{p}{(kT)^{5/2}}\left(\frac{h^2}{2\pi m^*}\right)^{3/2} \overset{?}{\ll} 1 \qquad (IIIC-A2)$$

APPENDIX IIIC-B

IONIZATION, DISSOCIATION, AND CHEMICAL ENERGY

The development in the unit was restricted to the consideration of pure substances in which the subject molecule (or atom) remained unaltered. In our brief consideration of the electronic mode (based on the one electron hydrogen atom), we concluded that this mode is not excited at ordinary temperatures, $T \ll \theta_{el}$. Thus it normally contributes little more than a constant to the properties of a molecular gas. It was on this basis that we ignored the electronic mode within the body of the unit.

I.   IONIZATION

When the temperature of a gas composed of hydrogen atoms is increased toward $\theta_{el,H}$, the electron of many of the atoms is excited to higher energy levels (or to larger Bohr

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Ans. A1. The result of Exmp. A1 can be written as the difference of two integrals. The second is negligible in the limit $T \gg \theta_{tr}$ and the first is available from Table IIIE-1.

$$Z_{tr} = \frac{\pi}{2}\left(\int_0^\infty q^2 e^{-q^2\theta_{tr}/T} dq - \int_0^{\sqrt{3}} q^2 e^{-q^2\theta_{tr}/T} dq\right) = \frac{\pi}{2}\frac{1}{4}\left[\pi\left(\frac{T}{\theta_{tr}}\right)^3\right]^{\frac{1}{2}} = \frac{1}{8}\left(\frac{\pi T}{\theta_{tr}}\right)^{3/2}$$

Ans. A2. The energy is defined as $\varepsilon = k\theta_{tr}q^2$. Thus $\varepsilon_{min} = 3k\theta_{tr}$, $\varepsilon_{max} = \infty$, $d\varepsilon = 2k\theta_{tr}qdq$. Thus

$$Z_{tr} = \frac{\pi}{2}\int_{\sqrt{3}}^\infty q^2 e^{-q^2\theta_{tr}/T} dr = \frac{\pi}{2}\int_{3k\theta_{tr}}^\infty \frac{\varepsilon}{k\theta_{tr}} e^{-\varepsilon/kT} \frac{d\varepsilon}{2(k\theta_{tr}\varepsilon)^{\frac{1}{2}}}$$

$$= \frac{\pi}{4}\frac{1}{(k\theta_{tr})^{3/2}}\int_{3k\theta_{tr}}^\infty \varepsilon^{\frac{1}{2}} e^{-\varepsilon/kT} d\varepsilon \quad \text{and} \quad g_{tr}(\varepsilon) = \frac{\pi}{4}\left[\frac{\varepsilon}{(k\theta_{tr})^3}\right]^{\frac{1}{2}}$$

orbits). As the temperature increases toward $\theta_{el,H}$, some atoms begin to lose their electron. The gas is *ionized* and becomes a *plasma*.[21]

The energy level series of a multielectron atom is as yet too difficult for analytic determination. However, for most atoms the values of $g_{el,\ell}$ and $\varepsilon_{el,\ell}$ for at least the first several levels have been measured spectroscopically (see the JANAF Tables). Like the hydrogen atom, at low temperatures the electrons of these atoms are unexcited; they occupy the lowest accessible states.[22] As the temperature level is increased some of the electrons are excited to higher levels. At still higher temperatures, some of the atoms would lose a single electron; they are then *singly ionized*. Upon further increases in temperature the atoms would successively lose a second and more electrons, and become doubly, triply, etc., ionized. For the hydrogen atom the ionization temperature is the coefficient of the entire electronic level series, $\theta_{el,H} = \theta_{I,H}$. For multielectron atoms no single constant is sufficient to describe the entire series. However, we can indicate the relative magnitude of this mode using a characteristic temperature defined from the energy for the first ionization state, $\theta_I = \Delta\varepsilon_{1,1}/k$. The values for a few atoms are listed in Table IIIC-B1. Notice that the ionization temperatures of the multielectron atoms listed are of the same order as that determined for the hydrogen atom, $\theta_I \sim 10^5 K$. The table does not list ionization temperatures for molecules, as most molecules tend to dissociate before they are appreciably ionized.

II. DISSOCIATION

A molecule is formed when a covalent or ionic force acts among the positively charged nuclei and negatively charged electrons of the participating atoms. That is, molecular bonds are formed by electronic interactions. A schematic representation of the first few energy levels of a representative diatomic molecule is shown in Fig. IIIC-B1. The figure also shows a few of the vibrational levels above each electronic minimum and a few much

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[21]The plasma state is relatively uncommon on earth. (It is present within a fluorescent tube, an electric arc, and a fusion reactor.) Nevertheless, the plasma state is the preponderant condition of matter in the universe, as most of the matter is concentrated in the stars.

[22]Free electrons are Fermions, thus at low temperature they fill up the states starting with the lowest level.

Ans. A3. The only parameter that depends on j in the series n_j/g_j is the magnitude of the energy of the successive levels, ε_j. Their order is defined to be sequentially increasing. Thus the first exponential in the series is the largest.

$$\frac{n_j}{g_j}\bigg|_{max} = \frac{n_1}{g_1} = \frac{N\,e^{-\varepsilon_1/kT}}{Z}$$

TABLE IIIC-B1. IONIZATION AND
DISSOCIATION TEMPERATURES

| IONIZATION TEMPERATURES		DISSOCIATION TEMPERATURES	
Symbol	θ_I (K)	Symbol	θ_d (K)
He	$2.855 \cdot 10^5$	H_2	$5.20 \cdot 10^4$
Ne	$2.500 \cdot 10^5$	N_2	$4.18 \cdot 10^4$
A	$1.830 \cdot 10^5$	O_2	$5.90 \cdot 10^4$
H	$1.579 \cdot 10^5$	Cl_2	$2.87 \cdot 10^4$
N	$1.690 \cdot 10^5$	CH	$4.03 \cdot 10^4$
O	$1.582 \cdot 10^5$	CO	$12.9 \cdot 10^4$
Cl	$1.512 \cdot 10^5$	HCl	$5.15 \cdot 10^4$
C	$1.308 \cdot 10^5$	NO	$7.53 \cdot 10^4$
S	$1.203 \cdot 10^5$	OH	$5.11 \cdot 10^4$
Na	$0.596 \cdot 10^5$		
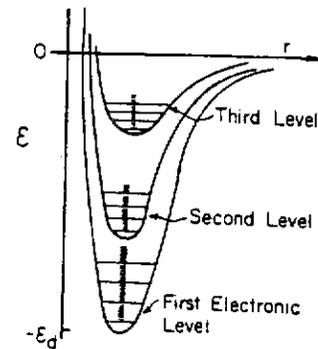
Fig. IIIC-B1. Electronic Levels of
a Diatomic Molecule (Schematic)

smaller rotational levels above each vibrational level. If the temperature is increased sufficiently, electrons will be excited to higher electronic levels. But like the atom, molecular electron excitation is not appreciable unless the temperature is raised to a very high level. At sufficiently high temperatures the molecule will dissociate. For the diatomic molecule represented in Fig. IIIC-B1, the dissociation level is represented by the depth of the potential well corresponding to the lowest electronic level, ε_d. Values of the dissociation energy for several atoms are reported in units of temperature in Table IIIC-B1, $\theta_d = \varepsilon_d/k$. Notice that molecular dissociation temperatures are about one order smaller than atomic ionization temperatures. After the molecules have dissociated, further increases in temperature cause the atoms to ionize.

We are now equipped to discuss chemical reactions. When atoms (or molecules) are combined to produce new molecular species the principal energy change results from the dissociation energy. To study this change, we must first formulate the electronic partition function for the molecule. For purposes of discussion, we arbitrarily choose the unionized atoms in their lowest electronic energy level as the zero level of electronic energy. Then the electronic partition function of the molecule can be written in the standard infinite series formulation. However at normal temperatures this partition function can be evaluated using low temperature limit, $T \ll \theta_d$, as consisting of its first term

$$Z_{el}|_{T \ll \theta_D} = \sum_{\ell=1}^{\infty} g_{el,\ell} \, e^{-\varepsilon_{el,\ell}/kT} \approx g_{el,1} \, e^{\theta_d/T} \qquad \text{IIIC-B1)}$$

The partition function allows us to formulate the electronic contribution to molecular properties (based on an atomic reference level).

Exercise B1. Formulate an expression for the energy, entropy, and specific heat of the electronic mode of a gas in the low temperature limit. (Answer on Pg. 34.)

Exer. B1 shows that the electronic contribution to the energy of a gas is a constant proportional to the dissociation temperature.

$$\bar{u}_{el}^{*}\big|_{T<<\theta_{d}} = - \bar{R}\,\theta_{d} \qquad\qquad\qquad (\text{IIIC-B2})$$

With this result we are able to determine the net energy change when a molecule is formed from its constituent atoms. For reference purposes these *formation reactions* are normally considered to occur at fixed temperature and pressure. Under these conditions the heat of the reaction is called the *enthalpy of formation*, $\Delta\bar{h}_{f}$.

<u>Example B1</u>. Determine the change in enthalpy when oxygen is formed from its constituent atoms at 298 K and atmospheric pressure.

The defining reaction is $2O \Rightarrow O_2$. Under these conditions both atomic and molecular oxygen are perfect gases. Thus the enthalpy change is

$$\Delta\bar{h}_{f}(T_o) = \bar{h}_{O_2}^{*}(T_o) - 2\bar{h}_{O}^{*}(T_o)$$

To determine the value we must use an absolute or a common reference base. We have chosen the atom in its lowest electronic level as a basis for our calculations.[23] Thus using the formulae of Table IIIC-1 and the data of Tables IIIC-2 and B1, we find

$$\bar{h}_{O_2}^{*}(298\ K) = \bar{R}\left\{\frac{7}{2}T + \theta_v\left[\frac{1}{2} + \frac{1}{\left(e^{\theta_v/T}-1\right)}\right] - \theta_d\right\} = 8.314\ J/(g\,mol\,K)\left\{\left(\frac{7}{2}\right)\cdot 298\ K\right.$$

$$\left.+ 3392\ K\left[\frac{1}{2} + \frac{1}{e^{(3392\ K/298\ K)}-1}\right] - 5.90\cdot 10^4\,K\right\} = -4.737\cdot 10^5\,J/(g\,mol)$$

$$\bar{h}_{O}^{*}(298\ K) = \frac{5}{2}\bar{R}T = \left(\frac{5}{2}\right)\cdot 8.314\ J/(g\,mol\,K)\cdot 298\ K = 6196\ J/(g\,mol)$$

Thus

$$\Delta\bar{h}_{f}(298\ K) = -4.588\cdot 10^5 - 2\cdot 6196 = -4.861\cdot 10^5\,J/(g\,mol)$$

Exmp. B1 affirms our expectation that the major portion of chemical energy results from the formation and or destruction of molecular bonds. Though we have only considered the formation reaction of a homonuclear diatomic molecule, the formation of compound molecules from unlike elements or new compounds from molecular reactants are simply extensions of the same techniques. Combustion processes are considered in Units VIB and C. The calculations for combustion analysis depend upon absolute property data developed by the methods of this unit.

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[23]The JANAF Tables use the elements in their natural state as the reference basis. Thus the enthalpy of formation of O_2 is defined as zero; but atomic oxygen has an enthalpy of reaction of opposite sign and half the value of the result obtained here.

<u>Ans. B1</u>.

$$\bar{u}_{el} = \bar{R}T^2\left(\frac{\partial \ln Z_{el}}{\partial T}\right)_{\bar{v}} = \bar{R}T^2\left[\frac{\partial}{\partial T}\left(g_{el,\ }e^{\theta_d/T}\right)\right]_{\bar{v}} = -\bar{R}\theta_d$$

$$\bar{c}_{v,el} = \left(\frac{\partial \bar{u}_{el}}{\partial T}\right)_{\bar{v}} = 0 \qquad \bar{s}_{el} = \frac{\bar{u}_{el}}{T} + \bar{R}\ln Z_{el} = \bar{R}\left[-\frac{\theta_d}{T} + \ln(g_{el,1}) + \frac{\theta_d}{T}\right] = \bar{R}\ln g_{el,1}$$

TABLE IIIC-1: CHARACTERISTICS OF GASEOUS MODES

Mode	Molecule	Limit	z_p	$\dfrac{\bar{u}_p^*}{R}$	$\dfrac{\bar{c}_{v,p}^*}{R}$	p_p	$\dfrac{\bar{s}_p^*}{R}$
Translation	All	$T \gg \Theta_{tr}$	$n_{\overline{v}}\left(\dfrac{2\pi m^o kT}{h^2}\right)^{3/2}$	$\dfrac{3}{2}T$	$\dfrac{3}{2}$	$\dfrac{RT}{v}$	$\dfrac{5}{2} + \ln\left[\dfrac{(kT)^{5/2}}{p}\left(\dfrac{2\pi m^*}{h^2}\right)^{3/2}\right]$
Rotation-Nuclear Spin	Monatomic	$T \ll \Theta_{ns}$	1	0	0	0	0
	Non Symmetric Linear	$T \gg \Theta_r$, $T \ll \Theta_{ns}$	$\dfrac{T}{\Theta_r}$	T	1	0	$1 + \ln\left(\dfrac{T}{\Theta_r}\right)$
	Symmetric Linear	$T \gg \Theta_r$, $T \ll \Theta_{ns}$	$\dfrac{T}{2\Theta_r}$	T	1	0	$1 + \ln\left(\dfrac{T}{2\Theta_r}\right)$
	Non Linear Polyatomic	$T \gg \Theta_r$, $T \ll \Theta_{ns}$	$\dfrac{\pi^{\frac{1}{2}}}{\sigma}\left(\dfrac{T}{\Theta_r}\right)^{3/2}$	$\dfrac{3}{2}T$	$\dfrac{3}{2}$	0	$\dfrac{3}{2}\left[1 + \ln\left(\dfrac{T}{\Theta_r}\right)\right] - \ln\left(\dfrac{\pi^{\frac{1}{2}}}{\sigma}\right)$
Vibration	Monatomic	None	1	0	0	0	0
	Diatomic	None	$\dfrac{e^{-\Theta_v/2T}}{(1 - e^{-\Theta_v/T})}$	$\Theta_v\left[\dfrac{1}{2} + \dfrac{1}{(e^{\Theta_v/T}-1)}\right]$	$\left(\dfrac{\Theta_v}{T}\right)^2\dfrac{e^{\Theta_v/T}}{(e^{\Theta_v/T}-1)^2}$	0	$\dfrac{\Theta_v/T}{(e^{\Theta_v/T}-1)} - \ln\left(1 - e^{-\Theta_v/T}\right)$
	Polyatomic	None	$\displaystyle\prod_{p=1}^{P}\dfrac{e^{-\Theta_{v,p}/2T}}{(1 - e^{-\Theta_{v,p}/T})}$	$\displaystyle\sum_{p=1}^{P}\Theta_{v,p}\left[\dfrac{1}{2} + \dfrac{1}{(e^{\Theta_{v,p}/T}-1)}\right]$	$\displaystyle\sum_{p=1}^{P}\left(\dfrac{\Theta_{v,p}}{T}\right)^2\dfrac{e^{\Theta_{v,p}/T}}{(e^{\Theta_{v,p}/T}-1)^2}$	0	$\displaystyle\sum_{p=1}^{P}\dfrac{\Theta_{v,p}/T}{(e^{\Theta_{v,p}/T}-1)} - \ln\left(1 - e^{-\Theta_{v,p}/T}\right)$

TABLE IIIC-2: ROTATIONAL AND VIBRATIONAL TEMPERATURES

Substance	Symbol	Θ_r (K)	σ	Θ_v (K)
Homonuclear Diatomic[a]				
Nitrogen	N_2	2.875	2	3392
Oxygen	O_2	2.079	2	2274
Hydrogen	H_2	87.55	2	6338
Chlorine	Cl_2	0.3465	2	807.3
Fluorine	F_2	1.286	2	1328
Bromine	Br_2	0.1164	2	425.1
Heteronuclear Diatomic[a]				
Carbon Monoxide	CO	2.777	1	3121
Nitric Oxide	NO	2.452	1	2739
Hydrogen Chloride	HCl	15.23	1	4302
Hydrogen Fluoride	HF	30.15	1	5954
Methylidyne	CH	20.80	1	4117
Sodium Chloride	NaCl	0.3121	1	523.2
Symmetric Linear Polyatomic[b]				
Carbon Dioxide	CO_2	0.5631	2	960.1(2) / 1932 / 3380
Methylene	CH_2	11.34	2	1602(2) / 3870 / 4604
Carbon Disulfide	CS_2	0.1568	2	570.9(2) / 946.8 / 2205
Acetylene	C_2H_2	1.693	2	880.0(2) / 1049(2) / 2840 / 4722 / 4854

Substance	Symbol	Θ_r (K)	σ	Θ_v (K)
Nonsymmetric Linear Polyatomic[b]				
Hydrogen Cyanide	HCN	2.137	1	1024(2) / 3022 / 4770
Potassium Cyanide	KCN	0.1570	1	297.8(2) / 466.2 / 3105
Nitrogen Monoxide	N_2O	0.6059	1	847.8(2) / 1836.7 / 3199.5
Nonlinear Polyatomic[b]				
Water	H_2O	0.2246	2	2294 / 5262 / 5404
Ammonia	NH_3	0.1233	3	1470 / 2433(2) / 5045 / 5147(2)
Methane	CH_4	0.07580	12	1879(3) / 2207(2) / 4196 / 4343(3)
Carbon Tetrachloride	CCl_4	0.01784	12	313.7(2) / 446.0(3) / 659.0 / 1142(3)

Data extracted from JANAF Thermochemical Tables, Second Ed. Issued, June (1971).

[a] Data reported as a wave number. The characteristic temperatures are determined as $\Theta_r = (hc/k)\cdot B_e$ and $\Theta_v = (hc/k)\cdot \omega_e$. (Anharmonic correction parameters are omitted.)

[b] Polyatomic vibrational data is reported as a wave number. Thus $\Theta_{v,p} = (hc/k)\cdot \omega_p$. Polyatomic rotational data given as either a wave number $\Theta_r = (hc/k)\cdot B_o$ or individual or product moments of inertia. $\Theta_r = [h/(8\pi^2 k)]\cdot I^{-1}$ or $\Theta_r = [h/(8\pi^2 k)]\cdot I^{-1/3}$.