10.40 Lecture 33 (Revised)
Computation of the properties of ideal gases (continued)

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Outline

- Degrees of freedom
- Computation of thermodynamic properties of polyatomic ideal gases, including diatomic ideal gases
- Summary of thermodynamic functions

33.1 Degrees of freedom

We have discussed *translational*, *electronic*, and *nuclear* degrees of freedom. Diatomic and polyatomic molecules have two additional internal degrees of freedom, *vibrational* and *rotational* degrees of freedom.

Excluding electronic and nuclear degrees of freedom, atoms and molecules have a total of $3N_{\text{atoms}}$ degrees of freedom, where N_{atoms} is the number of atoms in a molecule (or atom). Linear molecules have 2 rotational degrees of freedom and non-linear molecules have 3 rotational degrees of freedom. The rest of the degrees of freedom, $3N_{\text{atoms}}-5$ for linear molecules and $3N_{\text{atoms}}-6$ for non-linear molecules are considered to be vibrational degrees of freedom. From now on, we approximate these vibrational degrees of freedom as normal modes, i.e. modes of simple harmonic oscillators. We will also ignore nuclear degrees of freedom from now on.

33.2 Computation of thermodynamic properties of polyatomic ideal gases, including diatomic ideal gases

Recall that $Q = \frac{1}{N!}q^N$. First, we assume that all of the degrees of freedom are separable. Thus,

$$q(\underline{V},T) = q_t(\underline{V},T)q_r(T)q_v(T)q_e(T). \tag{1}$$

We discussed q_t and q_e in the previous lecture; we simply note here that if we choose the electronic energy of separated atoms as the electronic reference state, then we can define D_e as the dissociation energy, the energy needed to atomize the molecule.

Note that we are able to write q as a product of the individual q's of the degrees of freedom in (1) because we assume that the contributions of the individual degrees of freedom to the energy of the molecule are separable. That is, we assume that the energy can be written in the form

$$\varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e,$$

where ε_t is the energy of the translational degrees of freedom, ε_r is the rotational energy of the molecule, ε_v is the vibrational energy, and ε_e is the electronic energy. Under these conditions, the partition function q, which is given by

$$q = \sum_{\text{states } j} e^{-\beta\varepsilon_j}$$

can be written as

$$q = \sum_{\text{states } j} e^{-\beta(\varepsilon_{tj}+\varepsilon_{rj}+\varepsilon_{vj}+\varepsilon_{ej})} = \sum_{\text{states } j} e^{-\beta\varepsilon_{tj}} e^{-\beta\varepsilon_{rj}} e^{-\beta\varepsilon_{vj}} e^{-\beta\varepsilon_{ej}}. \tag{2}$$

However, since the separate degrees of freedom do not interact, we can write (2) as the product of sums over each type of degree of freedom:

$$\begin{aligned} q &= \sum_{\substack{\text{translational}\\ \text{states } j}} e^{-\beta\varepsilon_{tj}} \sum_{\substack{\text{rotational}\\ \text{states } k}} e^{-\beta\varepsilon_{rk}} \sum_{\substack{\text{vibrational}\\ \text{states } l}} e^{-\beta\varepsilon_{vl}} \sum_{\substack{\text{electronic}\\ \text{states } m}} e^{-\beta\varepsilon_{em}} \\ &= q_t q_r q_v q_e. \end{aligned}$$

Now, we need to compute q_r and q_v.

33.2.1 Vibrational degrees of freedom

From quantum mechanics, the energy levels of a harmonic oscillator are:

$$\begin{aligned} \varepsilon_n &= (n+\frac{1}{2})h\nu, \\ n &= 0,1,2,..., \end{aligned} \tag{3}$$

where h is Planck's constant and ν is the frequency. The vibrational partition function is then

$$q_v = \frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}},$$

where $\Theta_v = h\nu/k$. (You can verify this yourself.)

Then,

$$\begin{aligned} \underline{A}_v &= -kT\ln q_v^N = Nk\left[\frac{\Theta_v}{2T} + T\ln\left(1-e^{\Theta_v/T}\right)\right], \\ \underline{U}_v &= kT^2\left(\frac{\partial \ln q_v^N}{\partial T}\right) = Nk\left(\frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T}-1}\right), \\ \underline{C}_{Vv} &= \left(\frac{\partial \underline{E}}{\partial T}\right)_{V,N} = Nk\left(\frac{\Theta_v}{T}\right)^2 \frac{e^{\Theta_v/T}}{\left(e^{\Theta_v/T}-1\right)^2}, \end{aligned}$$

and

$$\underline{S}_v = \frac{\underline{E}_v - \underline{A}_v}{T} = Nk\left(\frac{\Theta_v}{e^{\Theta_v/T}-1}\right) - NkT\ln\left(1-e^{\Theta_v/T}\right).$$

We also emphasize that the terms $\frac{\Theta_v}{2}$ in the expressions for $\underline{U}_v$ and $\underline{A}_v$ above are a result of the fact that the ground state of the harmonic oscillator has a finite energy level as seen in equation 3. The term $\frac{1}{2}h\nu = \left(\frac{k\Theta_v}{2}\right)$ is called the *zero point energy* of the vibration.

We note that for a diatomic molecule, for example, the measured bond dissociation energy, D_0, is not the energy of atomization described at the beginning of the lecture. This is because the zero point energy adds a destabilizing contribution. Thus,

$$D_0 = D_e - \frac{1}{2}h\nu.$$

This can be easily generalized for polyatomic molecules.

33.3 Rotational degrees of freedom

From quantum mechanics, the energy levels of a rigid, linear rotator are

$$\begin{aligned} \varepsilon_j &= \frac{j(j+1)h^2}{8\pi^2 I}, \\ j &= 0, 1, 2, ..., \end{aligned}$$

where I is the moment of inertia. Note that for a diatomic molecule consisting of atoms 1 and 2, $I = \mu d^2$, where μ is the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2},$$

and d is the bond length. This can be generalized for polyatomic molecules. (See books on classical mechanics.)

For diatomic and non-linear polyatomic molecules, the rotational partition function is then

$$q_r = \sum_j \omega_j e^{-\beta\varepsilon_j} = \sum_j (2j+1)e^{-j(j+1)\Theta_r/T},$$

where

$$\Theta_r = \frac{h^2}{8\pi^2 Ik} \tag{4}$$

At sufficiently high temperatures T, we can replace the summation (4) with an integral, since the energy levels will be closely spaced together. Then we find

$$\begin{aligned} q_r &\rightarrow \int_o^\infty (2j+1)e^{-j(j+1)\Theta_r/T}dj \\ &= \frac{T}{\Theta_r} = \frac{8\pi^2 IkT}{h^2}. \end{aligned}$$

Note that in order to eliminate double counting, symmetry must be taken into account. The symmetry number is symbolized as σ, and for a diatomic molecule, $\sigma = 1$ if the molecule is unsymmetrical and $\sigma = 2$ if the molecule is symmetrical.

A non-linear polyatomic molecule will have 3 rotational degrees of freedom, and obviously the 3 different moments of inertia will almost always be different. For these species,

$$q_r = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_A kT}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_B kT}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_C kT}{h^2}\right)^{1/2}, \tag{5}$$

where σ is again the symmetry factor, which can take on many values, up to 12, and I_A, I_B, I_C are the three principle moments of inertia. (We ignore the derivation here, because it is somewhat complicated. It can be found in a book on classical mechanics.)

Formula (5) can be written more compactly using (4) as

$$q_r = \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}.$$

From this equation, we can derive the thermodynamic functions:

$$\begin{array}{c}\text{nonlinear}\\ \text{molecules only}\end{array}\begin{cases} \underline{A}_r = -NkT\ln\left[\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}\right] \\ \underline{E}_r = \frac{3}{2}NkT \\ \underline{C}_{Vr} = \frac{3}{2}Nk \\ \underline{S}_r = Nk\ln\left[\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3e^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}\right] \end{cases},$$

33.4 Summary of thermodynamic functions

Below is a summary of the thermodynamic functions, excluding nuclear and excited electronic degrees of freedom.

33.4.1 Monatomic ideal gas

$$\begin{aligned} \underline{A} &= -NkT\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{\underline{V}}{N}e\right]; \\ \underline{U} &= \frac{3}{2}NkT; \\ \underline{C}_V &= \frac{3}{2}Nk; \\ \underline{S} &= Nk\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{\underline{V}}{N}e^{5/2}\right]. \end{aligned}$$

Also, $\underline{H} = \underline{U} + P\underline{V} = \underline{U} + NkT$ and $\underline{G} = \underline{A} + P\underline{V} = \underline{A} + NkT$.

33.4.2 Diatomic and linear polyatomic ideal gas

$$\begin{aligned} -\frac{A}{kT} &= \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V}{N}e\right] + \ln\left[\frac{8\pi^2 IkTe}{\sigma h^2}\right] + \sum_{i=1}^{3N_{\text{atoms}}-5}\left[\frac{\Theta_v}{2T} + \ln\left(1 - e^{\Theta_v/T}\right)\right] + \frac{D_e}{kT} + \ln\omega_e; \\ \frac{U}{kT} &= \frac{3}{2} + \frac{2}{2} + \sum_{i=1}^{3N_{\text{atoms}}-5}\left[\frac{\Theta_v}{2T} + \frac{\Theta_v/T}{e^{\Theta_v/T}-1}\right] - \frac{D_e}{kT}; \\ \frac{C_V}{k} &= \frac{3}{2} + \frac{2}{2} + \sum_{i=1}^{3N_{\text{atoms}}-5}\left[\left(\frac{\Theta_v}{T}\right)^2\frac{e^{\Theta_v/T}}{\left(e^{\Theta_v/T}-1\right)^2}\right]; \\ \frac{S}{k} &= \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V}{N}e^{5/2}\right] + \ln\left[\frac{8\pi^2 IkTe}{\sigma h^2}\right] + \sum_{i=1}^{3N_{\text{atoms}}-5}\left[\frac{\Theta_v/T}{e^{\Theta_v/T}-1} - \ln\left(1 - e^{\Theta_v/T}\right)\right] + \ln\omega_e. \end{aligned}$$

Also, $H = U + PV = U + kT$ and $G = A + PV = A + kT$.

33.4.3 Non-linear polyatomic ideal gas

$$\begin{aligned}
-\frac{A}{kT} &= \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V}{N}e\right] + \ln\left[\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}\right] + \sum_{i=1}^{3N_{\text{atoms}}-6}\left[\frac{\Theta_v}{2T} + \ln\left(1 - e^{\Theta_v/T}\right)\right] + \frac{D_e}{kT} + \ln\omega_e;\\
\frac{U}{kT} &= \frac{3}{2} + \frac{3}{2} + \sum_{i=1}^{3N_{\text{atoms}}-6}\left[\frac{\Theta_v}{2T} + \frac{\Theta_v/T}{e^{\Theta_v/T}-1}\right] - \frac{D_e}{kT};\\
\frac{C_V}{k} &= \frac{3}{2} + \frac{3}{2} + \sum_{i=1}^{3N_{\text{atoms}}-6}\left[\left(\frac{\Theta_v}{T}\right)^2\frac{e^{\Theta_v/T}}{\left(e^{\Theta_v/T}-1\right)^2}\right];
\end{aligned}$$

and

$$\begin{aligned}
\frac{S}{k} = \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V}{N}e^{5/2}\right] + \ln\left[\frac{\pi^{1/2}e^{3/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}\right]\\
+ \sum_{i=1}^{3N_{\text{atoms}}-6}\left[\frac{\Theta_v/T}{e^{\Theta_v/T}-1} - \ln\left(1 - e^{\Theta_v/T}\right)\right] + \ln\omega_e.
\end{aligned}$$

Also, $H = U + PV = U + kT$ and $G = A + PV = A + kT$.