Diatomic Gases

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Diatomic Gases

- We have already obtained the translational and electronic partition functions
- Now we must determine molecular partition functions for rotation and vibration

$$\ln Q = e^{-\gamma} q_{tr} q_e q_v q_r$$

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Rotation

The energy and degeneracy are:

$$\varepsilon_r = k\Theta_r J(J+1) \qquad g_J = 2J+1$$

so that

$$q_r = \sum_J (2J+1) e^{-\frac{\varepsilon_J}{kT}} = \sum_J (2J+1) e^{-\frac{\Theta_r}{T} J(J+1)}$$

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Expanding the exponential

$$q_r = \frac{T}{\Theta_r}\left[1 + \frac{1}{3}\frac{\Theta_r}{T} + \frac{1}{15}\left(\frac{\Theta_r}{T}\right)^2 + \cdots\right]$$

Thus, when $T >> \Theta_r$

$$q_r = \frac{T}{\Theta_r}$$

Since the rotational temperature is typically 100K or less, this is a pretty good approximation most of the time.

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There is one complication. For homonuclear molecules such as H_2, O_2, N_2 etc., symmetry requirements place restrictions on the possible values of the rotational quantum number. In fact, only even or odd ones are allowed, so that generally

$$q_r = \frac{1}{\sigma}\frac{T}{\Theta_r}$$

where σ is a symmetry factor, and

$\sigma = 1$ for heteronuclear

$\sigma = 2$ for homonuclear

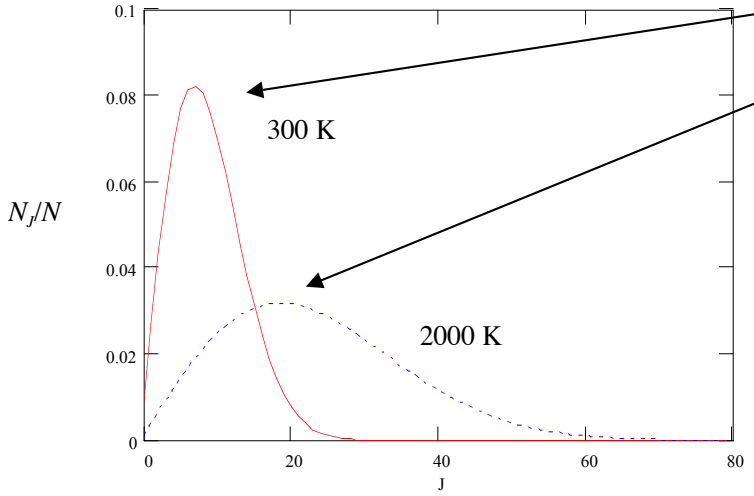
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The fraction of molecules in the *J*th rotational state is then

$$\frac{N_J}{N} = \frac{g_J e^{-J(J+1)\frac{\Theta_r}{T}}}{q_r(T)}$$

This results in a peaked distribution

$$J_{\max} \approx \left(\frac{T}{2\Theta_r}\right)^{1/2}$$



Equilibrium Rotational Population Distribution for CO

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Vibration

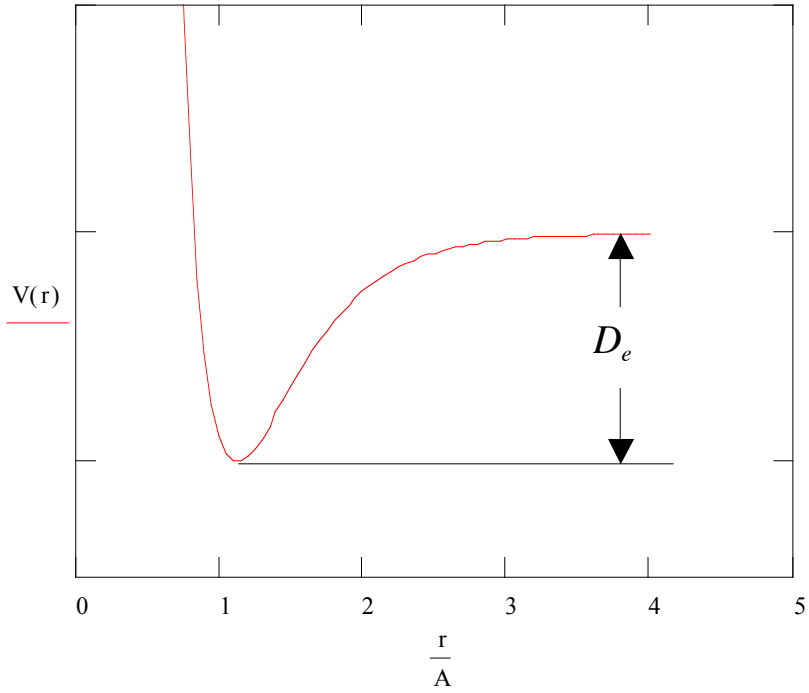
The vibration energy is (degeneracy is unity)

$$\varepsilon_v = h\nu_v(v + 1/2)$$

However, if we wish to deal with mixtures, there is an issue of referencing.

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The potential function of a real diatomic molecule will look similar to that shown below.



In this coordinate system, the absolute energy of vibration is set to zero when there is a complete separation of the atoms that make up the molecule.

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This makes sense because

$$PE = -\int_{r}^{\infty} F(r)dr$$

and as the atoms approach from a distance, there is initially no force and the potential energy is zero.

Because of this, and because referencing is important when working with reacting mixtures, it is usual to set the same zero reference for each molecule when calculating the partition function.

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Therefore, we will write the vibrational energy as

$$\varepsilon_v = h\nu_v(v + 1/2) - D_e$$

D_e is called the electronic binding energy, and is the total depth of the potential well.

The partition function thus becomes

$$q_v = e^{\frac{D_e}{kT}} \sum_v e^{-\frac{h\nu(v+1/2)}{kT}} = e^{\frac{D_e}{kT}} \sum_v e^{-\frac{\Theta_v}{T}(v+1/2)}$$

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The sum can be expanded as

$$\sum_v e^{-\frac{\Theta_v}{T}(v+1/2)} = \sum_v e^{-\frac{\Theta_v}{2T}(2v+1)} = e^{-\frac{\Theta_v}{2T}}\left\{1 + e^{-\frac{\Theta_v}{T}} + e^{-2\frac{\Theta_v}{T}} + \cdots\right\}$$

and the term is the brackets is a binomial expansion. Thus, the partition function can be written

$$q_v = e^{\frac{D_e}{kT}} \frac{e^{-\frac{\Theta_v}{2T}}}{1 - e^{-\frac{\Theta_v}{T}}} = e^{\frac{D_e}{kT}} \frac{1}{2Sinh\left(\Theta_v / 2T\right)}$$

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Substituting all the molecular partition functions into the full partition function, we have the Fundamental Relation for $T >> \Theta_r$ and $q_e = g_e$

$$S\left[\frac{1}{T}, -\frac{\mu}{T}\right] = e^{-\frac{\mu}{kT}} \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V\left(\frac{T}{\sigma\Theta_r}\right) \frac{e^{\frac{D_e}{kT}}}{2Sinh(\Theta_v / 2T)} g_e$$

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If we evaluate the equations of state, we would find that the perfect gas law still holds, and that the energy per molecule is

$$u = \frac{3}{2}kT + kT + \left\{ -D_e + \frac{k\Theta_v}{2} Coth \frac{\Theta_v}{T} \right\}$$

Entropy is

$$s = \frac{S}{N} = k \left\{ \frac{7}{2} + \left(\frac{\Theta_v}{2T} Coth \frac{\Theta_v}{2T} - D_e \right) - \frac{\mu}{kT} \right\}$$

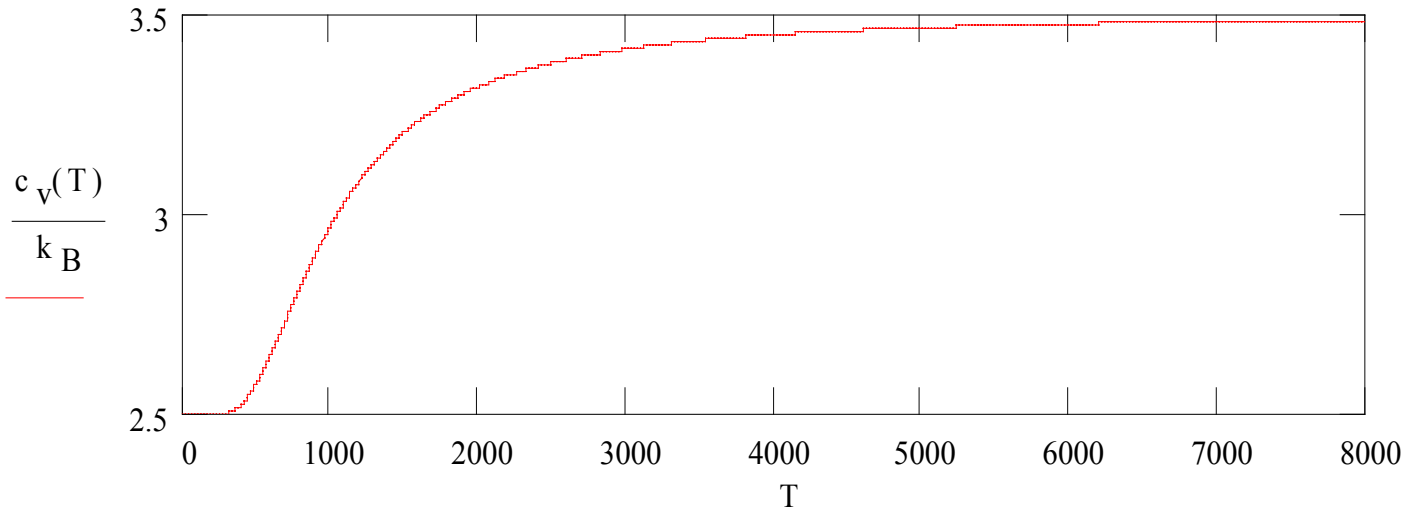
Specific heat is

$$c_v = k \left[\frac{3}{2} + 1 + \left\{ \frac{\Theta_v / 2T}{Sinh(\Theta_v / 2T)} \right\}^2 \right]$$

$$tr \quad rot \qquad vib$$

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The temperature dependence of the specific heat is



For T << Θ_D, $c_v \longrightarrow 5/2$ For T >> Θ_D, $c_v \longrightarrow 7/2$

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The separation of the rotational and vibrational partition functions is only strictly allowed when the two motions are completely independent. Recall that, for real molecules

$$G(v)+F(J)=\omega_e(v+\frac{1}{2})-\omega_e x_e(v+\frac{1}{2})^2+\omega_e y_e(v+\frac{1}{2})^3-\ldots$$
$$+B_v J(J+1)-D_v J^2(J+1)^2+\ldots$$

Then the combined partition function must be evaluated numerically

$$q_{v,r}=\frac{1}{\sigma}\sum_v\sum_J(2J+1)e^{-(hc/kT)\left[G(v)+F_v(J)\right]}$$

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