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ME 501**Exam #2****November 15, 2013****Prof. Lucht****ME 256****1. POINT DISTRIBUTION**

Problem #1	30 points	_____
Problem #2	35 points	_____
Problem #3	35 points	_____

2. EXAM INSTRUCTIONS

- Write your name on each sheet.
- This exam is closed book and closed notes.
- Several equation sheets are attached.
- When working the problems, list all assumptions, and begin with the basic equations.
- If you do not have time to complete evaluation of integrals or of terms numerically, remember that the significant credit on each problem will be given for setting up the problem correctly and/or obtaining the correct analytical solution.

1. (30 points) One (1.0) kmol of gaseous CO is contained in a piston cylinder system tank at a pressure of 10^5 Pa (1.00 bar) at a temperature of 300 K (state 1). The temperature of the piston-cylinder system is raised to a temperature of 2000 K and a pressure of 4×10^5 Pa (4.00 bars) (state 2) by heat transfer. Assume that CO exhibits ideal gas behavior at both states 1 and 2, and that the CO does not dissociate. Recall that CO has a $^1\Sigma^+$ ground electronic level.

Assuming that CO is a rigid-rotator and harmonic oscillator, calculate the entropy change $S_2 - S_1$ (in J/K or kJ/K) for the process.

For CO:	$\theta_{rot}(K)$	$\theta_{vib}(K)$	m (amu)
	2.78	3120	28.01

Solution:

$$S_2 - S_1 = (S_2 - S_1)_{tr} + (S_2 - S_1)_{rot} + (S_2 - S_1)_{vib} + (S_2 - S_1)_{elec} \quad \boxed{+3}$$

$$(S_2 - S_1)_{elec} = 0$$

$$S_{trans} = Nk_B \left\{ \frac{5}{2} \ln T - \ln P + \ln \left[\left(\frac{2\pi m}{h^2} \right)^{3/2} k_B^{5/2} \right] + \frac{5}{2} \right\} \quad \boxed{+2}$$

$$(S_2 - S_1)_{trans} = Nk_B \left\{ \frac{5}{2} \ln \left(\frac{T_2}{T_1} \right) - \ln \left(\frac{P_2}{P_1} \right) \right\} = Nk_B \left\{ 2.5 \ln \left(\frac{2000}{300} \right) - \ln \left(\frac{4}{1} \right) \right\}$$

$$(S_2 - S_1)_{tr} = 3.357 Nk_B \quad \boxed{+5}$$

$$S_{int} = Nk_B \ln Z_{int} + \frac{E_{int}}{T} \quad \boxed{+2}$$

$$Z_{rot} = \frac{T}{\theta_{rot}} \quad E_{rot} = Nk_B T \quad \frac{E_{rot}}{T} = Nk_B$$

$$(S_2 - S_1)_{rot} = Nk_B \ln \left(\frac{T_2}{T_1} \right) = Nk_B \ln \left(\frac{2000}{300} \right) = 1.897 Nk_B \quad \boxed{+5}$$

$$Z_{vib} = \frac{1}{1 - \exp(-\theta_{vib}/T)} \quad \theta_{vib} = 3120 \text{ K}$$

$$Z_{vib1} = \frac{1}{1 - \exp(-3120/300)} = 1.000 \quad Z_{vib2} = \frac{1}{1 - \exp(-3120/2000)} = 1.266$$

$$E_{vib} = U_{vib} = \frac{N k_B \theta_{vib}}{\exp(\theta_{vib}/T) - 1}$$

$$E_{vib1} = U_{vib1} = N k_B \frac{3120 \text{ K}}{\exp(3120/300) - 1} = N k_B (9.495 \times 10^{-2} \text{ K})$$

$$E_{vib2} = U_{vib2} = N k_B \frac{3120 \text{ K}}{\exp(3120/2000) - 1} = N k_B (830.0 \text{ K})$$

$$(S_2 - S_1)_{vib} = N k_B \ln \left(\frac{Z_{vib2}}{Z_{vib1}} \right) + \frac{E_{vib2}}{T_2} - \frac{E_{vib1}}{T_1} = N k_B \left[\ln(1.266) + \frac{830.0}{2000} - \frac{9.495 \times 10^{-2}}{300} \right]$$

$$(S_2 - S_1)_{vib} = 0.6505 N k_B \quad \boxed{+10}$$

$$S_2 - S_1 = N k_B (3.357 + 1.897 + 0.6505) = (6.022 \times 10^{26}) (1.381 \times 10^{-23} \text{ J / K}) (5.905)$$

$$\boxed{S_2 - S_1 = 4.910 \times 10^4 \text{ J / K} = 49.10 \text{ kJ / K}} \quad \boxed{+3}$$

2. (35 points) A system has four energy levels with energies and degeneracies as shown in the diagram. A spectroscopic measurement is performed and it is determined that the populations of levels 1 and 2 are equal.
- (a) What is the assembly temperature? Assume thermodynamic equilibrium and corrected-Maxwell-Boltzmann statistics.
- (b) What is the value of the partition function for the assembly? Assume corrected-Maxwell-Boltzmann statistics. Note: this system **does not have** translational, rotational, etc. energy levels. It has only the energy levels specified. Note that the energy level spacing is not to scale in the diagram below. Remember to write down the values of the individual terms in the partition function summation for use in part (c).
- (c) For an assembly of 10^{10} particles, find the assembly energy E (in J). Assume corrected-Maxwell-Boltzmann statistics.

	j	ε_j/k_B (K)	g_j
—————	3	900	2×10^{14}
—————	2	400	10^{14}
—————	1	100	5×10^{13}
—————	0	0	2×10^{13}

Solution:

(a)

$$\frac{N_2}{N_1} = \frac{g_2 \exp\left(-\frac{\varepsilon_2}{k_B T}\right)}{g_1 \exp\left(-\frac{\varepsilon_1}{k_B T}\right)} = 1 \quad g_2 \exp\left(-\frac{\varepsilon_2}{k_B T}\right) = g_1 \exp\left(-\frac{\varepsilon_1}{k_B T}\right) \quad \boxed{+7}$$

$$\ln g_2 - \left(\frac{\varepsilon_2}{k_B}\right)\left(\frac{1}{T}\right) = \ln g_1 - \left(\frac{\varepsilon_1}{k_B}\right)\left(\frac{1}{T}\right) \Rightarrow \ln\left(\frac{g_2}{g_1}\right) = \left[\left(\frac{\varepsilon_2}{k_B}\right) - \left(\frac{\varepsilon_1}{k_B}\right)\right]\left(\frac{1}{T}\right)$$

$$T = \frac{\left(\frac{\varepsilon_2}{k_B}\right) - \left(\frac{\varepsilon_1}{k_B}\right)}{\ln\left(\frac{g_2}{g_1}\right)} = \frac{400\text{ K} - 100\text{ K}}{\ln\left(\frac{10^{14}}{5 \times 10^3}\right)} = \frac{300\text{ K}}{\ln 2}$$

$$\boxed{T = 432.8\text{ K}} \quad \boxed{+8}$$

(b)

$$Z = \sum_j g_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right) \quad T = 432.8\text{ K}$$

$$Z = 2 \times 10^{13} + 5 \times 10^{13} \exp\left(-\frac{100}{432.8}\right) + 10^{14} \exp\left(-\frac{400}{432.8}\right) + 2 \times 10^{14} \exp\left(-\frac{900}{432.8}\right)$$

$$Z = 2 \times 10^{13} + 3.968 \times 10^{13} + 3.968 \times 10^{13} + 2.500 \times 10^{13}$$

$$\boxed{Z = 1.244 \times 10^{14}} \quad \boxed{+10}$$

(c)

$$N_0 = \frac{N}{Z} g_0 \exp\left[-\frac{(\varepsilon_0/k_B)}{T}\right] = \left(\frac{10^{10}}{1.244 \times 10^{14}}\right) 2 \times 10^{13} = (8.039 \times 10^{-5})(2 \times 10^{13}) = 1.608 \times 10^9$$

$$N_1 = (8.039 \times 10^{-5})(3.968 \times 10^{13}) = 3.190 \times 10^9$$

$$N_2 = (8.039 \times 10^{-5})(3.968 \times 10^{13}) = 3.190 \times 10^9$$

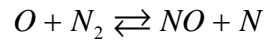
$$N_2 = (8.039 \times 10^{-5})(2.500 \times 10^{13}) = 2.010 \times 10^9$$

$$E = \sum_j N_j \varepsilon_j = k_B \sum_j N_j \left(\frac{\varepsilon_j}{k_B}\right) = (1.381 \times 10^{-23} \text{ J/K}) \left[(1.608 \times 10^9)(0) + (3.190 \times 10^9)(100\text{ K}) \right. \\ \left. + (3.190 \times 10^9)(400\text{ K}) + (2.010 \times 10^9)(900\text{ K}) \right] \quad \boxed{+10}$$

$$\boxed{E = 4.701 \times 10^{-11} \text{ J}}$$

ME 501 Exam #2 11/15/2013 Name _____

3. (35 points) A rigid pressure vessel with a volume of 1 m^3 contains 0.1 kmols of diatomic oxygen (O_2) and 0.1 kmols of diatomic nitrogen (N_2) at 300K. The gas is then heated to 3000 K. At 3000 K, find the equilibrium ratio $\frac{N_N N_{NO}}{N_O N_{N_2}}$ for the reaction. Consider the reaction



Assume that the molecules are rigid rotators and harmonic oscillators, and use the following data:

Species	$\theta_{\text{rot}}(\text{K})$	$\theta_{\text{vib}}(\text{K})$	(D_0/k_B) (K)
N_2	2.875	3390	113,000
NO	2.452	2740	75,300

For the calculation of the electronic partition functions, consider the following electronic levels:

O: **Level 0** [$g_0 = 5$, $(\epsilon_0/k_B) = 0 \text{ K}$], **Level 1** [$g_1 = 3$, $(\epsilon_1/k_B) = 228 \text{ K}$],

Level 2 [$g_2 = 1$, $(\epsilon_2/k_B) = 325 \text{ K}$]

N_2 : **Level 0** [$g_0 = 1$, $(\epsilon_0/k_B) = 0 \text{ K}$]

NO: **Level 0** [$g_0 = 2$, $(\epsilon_0/k_B) = 0 \text{ K}$], **Level 1** [$g_1 = 2$, $(\epsilon_1/k_B) = 174 \text{ K}$]

N: **Level 0** [$g_0 = 2$, $(\epsilon_0/k_B) = 0 \text{ K}$]

For masses use:

O: 16 amu

N_2 : 28 amu

NO: 30 amu

N: 14 amu

Solution:

For the reaction $\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$,

$$\frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} = \frac{Z_C^{\nu_C} Z_D^{\nu_D}}{Z_A^{\nu_A} Z_B^{\nu_B}} \exp\left(-\frac{\epsilon_R}{k_B T}\right), \quad \epsilon_R = +\nu_A D_{0,A} + \nu_B D_{0,B} - \nu_C D_{0,C} - \nu_D D_{0,D}$$

For the equilibrium reaction $\text{O} + \text{N}_2 \rightleftharpoons \text{NO} + \text{N}$,

$$\frac{\varepsilon_R}{k_B} = \frac{D_{0,N_2}}{k_B} - \frac{D_{0,NO}}{k_B} = 113,000 - (75,300) = 37,700 \text{ K}$$

Calculate the ratio of partition functions:

$$\frac{Z_C^{V_C} Z_D^{V_D}}{Z_A^{V_A} Z_B^{V_B}} = \frac{Z_{NO} Z_N}{Z_O Z_{N_2}} = \frac{Z_N}{Z_O} \frac{Z_{NO}}{Z_{N_2}}$$

For the atoms:

$$Z = Z_{trans} Z_{elec}$$

$$\frac{Z_N}{Z_O} = \left(\frac{Z_{trans,N}}{Z_{trans,O}} \right) \left(\frac{Z_{elec,N}}{Z_{elec,O}} \right) \quad \boxed{+2}$$

$$= r_{trans} r_{elec}$$

For the molecules

$$Z = Z_{trans} Z_{elec} Z_{vib} Z_{rot}$$

$$\frac{Z_{NO}}{Z_{N_2}} = \left(\frac{Z_{trans,NO}}{Z_{trans,N_2}} \right) \left(\frac{Z_{elec,NO}}{Z_{elec,N_2}} \right) \left(\frac{Z_{vib,NO}}{Z_{vib,N_2}} \right) \left(\frac{Z_{rot,NO}}{Z_{rot,N_2}} \right) \quad \boxed{+3}$$

$$= q_{trans} q_{elec} q_{vib} q_{rot}$$

$$Z_{elec,O} = 5 + 3 \exp \left[-\frac{(\varepsilon_1/k_B)}{T} \right] + \exp \left[-\frac{(\varepsilon_2/k_B)}{T} \right]$$

$$= 5 + 3 \exp \left[-\frac{228}{3000} \right] + \exp \left[-\frac{325}{3000} \right] = 5 + 2.780 + 0.8973 = 8.678$$

$$Z_{elec,N} = 2$$

$$Z_{elec,N_2} = 1$$

$$Z_{elec,NO} = 2 + 2 \exp \left[-\frac{(\varepsilon_1/k_B)}{T} \right] = 2 + 2 \exp \left[-\frac{174}{3000} \right] = 2 + 1.887 = 3.887$$

$$r_{elec} q_{elec} = \frac{(2)(3.887)}{(8.678)(1)} = 0.8958 \quad \boxed{+5}$$

For the vibrational partition function we must use the form where ZPE is not included to be consistent with our choice of D_0 instead of D_e for the dissociation energy.

$$Z_{vib,NO} = \frac{1}{[1 - \exp(-\theta_{vib,NO}/T)]} = \frac{1}{[1 - \exp(-2740/3000)]} = 1.670$$

$$Z_{vib,N_2} = \frac{1}{[1 - \exp(-\theta_{vib,N_2}/T)]} = \frac{1}{[1 - \exp(-3390/3000)]} = 1.477$$

$$q_{vib} = \frac{Z_{vib,NO}}{Z_{vib,N_2}} = \frac{(1.670)}{(1.477)} = 1.131 \quad \boxed{+5}$$

For the rotational partition functions:

$$Z_{rot,NO} = \frac{T}{\sigma_{NO} \theta_{rot,NO}} \quad \sigma_{NH} = 1$$

$$Z_{rot,N_2} = \frac{T}{\sigma_{N_2} \theta_{rot,N_2}} \quad \sigma_{N_2} = 2$$

$$q_{rot} = \frac{\left(\frac{T}{\sigma_{NO} \theta_{rot,NO}} \right)}{\left(\frac{T}{\sigma_{N_2} \theta_{rot,N_2}} \right)} = \frac{\theta_{rot,N_2} \sigma_{rot,N_2}}{\theta_{rot,NO} \sigma_{rot,NO}} = \frac{(2.875 \text{ K})}{(2.452 \text{ K})} (2) = 2.345 \quad \boxed{+5}$$

Note that this ratio does not depend on temperature.

Now for the translational mode:

$$Z_{trans,i} = \left(\frac{2\pi m_i k_B T}{h^2} \right)^{3/2}$$

$$r_{trans} q_{trans} = \frac{Z_{trans,N} Z_{trans,NO}}{Z_{trans,O} Z_{trans,N_2}} = \left(\frac{m_N m_{NO}}{m_O m_{N_2}} \right)^{3/2} = \left[\frac{(14 \text{ amu})(30 \text{ amu})}{(16 \text{ amu})(28 \text{ amu})} \right]^{3/2} = 0.9077 \quad \boxed{+5}$$

Now we can calculate the ratio of number of molecules of the species in the assembly:

$$\frac{N_{NO}N_N}{N_O N_{N_2}} = \frac{Z_{NO}Z_N}{Z_O Z_{N_2}} \exp\left[-\frac{(\varepsilon_R/k_B)}{T}\right]$$

$$\frac{Z_{NO}Z_N}{Z_O Z_{N_2}} = (r_{trans} q_{trans})(r_{elec} q_{elec}) q_{vib} q_{rot} = (0.9077)(0.8948)(1.131)(2.345) = 2.154$$

$$\exp\left[-\frac{(\varepsilon_R/k_B)}{T}\right] = \exp\left[-\frac{37,700}{3000}\right] = 3.486 \times 10^{-6} \quad \boxed{+5}$$

$$\boxed{\frac{N_{NO}N_N}{N_O N_{N_2}} = (2.154)(3.486 \times 10^{-6}) = 7.509 \times 10^{-6}} \quad \boxed{+5}$$

Equation Sheets

TdS Equations: $du = T ds - P dv, \quad h = u + P v, \quad g = h - T s, \quad f = u - T s$

$$[dg]_T = RT [d(\ln f)]_T \quad ds = \delta Q_{rev} / T$$

First Law - Closed System: $\Delta U = Q - W$ neglecting KE, PE

First Law - Open System: neglecting KE, PE

$$\dot{Q} - \dot{W}_{shaft} = \frac{d}{dt} \int_{CV} u \rho d\forall + \int_{CS} (u + P v) \rho \vec{V} \cdot d\vec{A}$$

Specific Heats: $c_p = \left(\frac{\partial h}{\partial T} \right)_p = T \left(\frac{\partial s}{\partial T} \right)_p$; $c_v = \left(\frac{\partial u}{\partial T} \right)_v = T \left(\frac{\partial s}{\partial T} \right)_v$

Schrödinger wave equation: $i \hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}, t) \Psi(\vec{r}, t)$

Time-independent Schrödinger wave equation: $-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = \varepsilon \psi(\vec{r})$

Normalization Condition: $1 = \iiint_{\forall} \Psi^*(\vec{r}, t) \Psi(\vec{r}, t) d\forall$ *three-dimensional form*

Dynamical Variable

Operator

$$\vec{r}$$

$$\vec{r}_{op} = \vec{r}$$

$$\vec{p}$$

$$\vec{p}_{op} = -i \hbar \nabla$$

$$p_{x,op} = -i \hbar \frac{\partial}{\partial x}$$

$$\vec{p}^2 = \vec{p} \cdot \vec{p}$$

$$\vec{p}_{op}^2 = -\hbar^2 \nabla^2$$

$$\varepsilon$$

$$\varepsilon_{op} = i \hbar \frac{\partial}{\partial t}$$

$$B(\vec{r}, \vec{p})$$

$$B_{op} = B(\vec{r}, -i \hbar \nabla)$$

$$\nabla = \hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} + \hat{z} \frac{\partial}{\partial z} \quad \text{Cartesian coord}$$

$$\nabla = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \quad \text{spherical coord}$$

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \quad \text{Cartesian coord}$$

$$\nabla^2 \psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \quad \text{Spherical coord}$$

Expectation Values: $\langle B \rangle = \iiint_{\forall} \Psi^*(\vec{r}, t) [B_{op} \Psi(\vec{r}, t)] d\forall \quad \text{three-dimensional form}$

$$d\forall = dx dy dz \quad \text{Cartesian coord,}$$

$$d\forall = r^2 \sin \theta dr d\theta d\phi \quad \text{Spherical coord}$$

$$\langle B \rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t) [B_{op} \Psi(x, t)] dx \quad \text{one-dimensional form}$$

$$\langle B^2 \rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t) \{ B_{op} [B_{op} \Psi(x, t)] \} dx \quad \text{one-dimensional form}$$

Molecular Energy Levels

$$\frac{\mathcal{E}_{vib}}{hc} = G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 \quad \text{with zero-point energy included}$$

$$\frac{\mathcal{E}_{vib}}{hc} = G(v) = \omega_e v - \omega_e x_e (v^2 + v) \quad \text{zero-point energy subtracted, } G(0) = 0$$

$$\frac{\mathcal{E}_{rot}}{hc} = F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2$$

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right) \quad D_e = \frac{4B_e^3}{\omega_e^2} = D_v \quad \text{for all } v$$

Degeneracies: $g_{rot} = 2J + 1 \quad g_{vib} = 1$

Rigid Rotator, Harmonic Oscillator

$$\frac{\mathcal{E}_{rot}}{hc} = F(J) = B_e J(J+1) \quad \frac{\mathcal{E}_{rot}}{k_B} = \theta_{rot} J(J+1) \quad \frac{\mathcal{E}_{vib}}{hc} = G(v) = \omega_e \left(v + \frac{1}{2} \right)$$

$$\frac{\mathcal{E}_{vib}}{hc} = G(v) = \omega_e \left(v + \frac{1}{2} \right) \quad \frac{\mathcal{E}_{vib}}{k_B} = \theta_{vib} \left(v + \frac{1}{2} \right) \quad \text{ZPE included}$$

$$\frac{\mathcal{E}_{vib}}{hc} = G(v) = \omega_e v \quad \frac{\mathcal{E}_{vib}}{k_B} = \theta_{vib} v \quad \text{ZPE not included}$$

Characteristic Temperatures:

$$\theta_{rot} = \frac{hc}{k_B} B_e \quad \theta_{vib} = \frac{hc}{k_B} \omega_e \quad \frac{hc}{k_B} = 1.439 \frac{K}{cm^{-1}}$$

Term Symbols Atomic: $2S+1L_J$, $J = (L+S), (L+S-1), \dots, |L-S|$

Term Symbol:	S	P	D	F	G....
L:	0	1	2	3	4.....

Term Symbols Molecular: $2S+1\Lambda_{\Lambda+\Sigma}$

Term Symbol	Σ	Π	Δ	Φ	Γ
	0	1	2	3	4

$$\mu = \frac{m_A m_B}{m_A + m_B} = \text{reduced mass}$$

Boltzmann Relation: $S = k_B \ln(W_{tot}) \cong k_B \ln(W_{mp})$

Number of Microstates in a Macrostate

$$\ln(W_{m,CMB}) = \sum_j \left[N_j \ln \left(\frac{g_j}{N_j} \right) + N_j \right] = N + \sum_j N_j \ln \left(\frac{g_j}{N_j} \right)$$

$$\ln W_{m,FD} = \sum_j \left[N_j \ln \left(\frac{g_j - N_j}{N_j} \right) - g_j \ln \left(\frac{g_j - N_j}{g_j} \right) \right]$$

$$\ln W_{m,BE} = \sum_j \left[N_j \ln \left(\frac{g_j + N_j}{N_j} \right) + g_j \ln \left(\frac{g_j + N_j}{g_j} \right) \right]$$

Partition Function, Boltzmann Distribution Relations

$$Z = \sum_j g_j \exp(-\varepsilon_j/k_B T) \quad , \quad N_j = N \frac{g_j \exp(-\varepsilon_j/k_B T)}{Z} \quad , \quad g_j = \text{level degeneracy}$$

$$N = \sum_j N_j \quad , \quad E = \sum_j N_j \varepsilon_j$$

$$Z_{trans} = \forall \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

$$Z_{rot} = \frac{1}{\sigma} \left(\frac{T}{\theta_{rot}} \right) \quad \text{for rigid rotator, } T \gg \theta_{rot} \quad , \quad \sigma = 2 \text{ for homonuclear molecule,}$$

$\sigma = 1$ for heteronuclear molecule,

$$Z_{vib} = \frac{\exp(-\theta_{vib}/2T)}{1 - \exp(-\theta_{vib}/T)} \quad \text{[with zero-point energy included in G(v)]}$$

$$Z_{vib} = \frac{1}{1 - \exp(-\theta_{vib}/T)} \quad \text{[without zero-point energy included in G(v)]}$$

$$Z_{nuc} = (2I_A + 1)(2I_B + 1) \quad \text{molecule AB, nuclear spins } I_A, I_B$$

$$Z_{nuc} = (2I_A + 1) \quad \text{atom A, nuclear spin } I_A$$

Rotational Distributions, Homonuclear Molecule

$$\frac{N_{\ell v J}}{N_{\ell v}} = (NSSW) \frac{(2J+1)}{Z_{rot} Z_{nuc}} \exp[-J(J+1)\theta_{rot}/T] \quad \text{rigid rotator}$$

Chemical Equilibrium

For the general reaction $\nu_A A + \nu_B B \Leftrightarrow \nu_C C + \nu_D D$

$$\frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} = \frac{Z_C^{\nu_C} Z_D^{\nu_D}}{Z_A^{\nu_A} Z_B^{\nu_B}} \exp\left(-\frac{\varepsilon_R}{k_B T}\right) \quad ; \quad \varepsilon_R = \nu_A D_{0A} + \nu_B D_{0B} - \nu_C D_{0C} - \nu_D D_{0D}$$

Statistical Thermodynamic Property Calculations: CMB Statistics

$$E = U = N k_B T^2 \left[\frac{\partial (\ln Z)}{\partial T} \right]_{\vee}$$

$$E_{trans} = U_{trans} = \frac{3}{2} N k_B T$$

$$E_{rot} = U_{rot} = N k_B T \quad \text{for rigid rotator, } T \gg \theta_{rot}$$

$$E_{vib} = U_{vib} = N k_B \left[\frac{\theta_{vib}}{2} + \frac{\theta_{vib}}{\exp(\theta_{vib}/T) - 1} \right] \quad \text{zero-point energy included}$$

$$E_{vib} = U_{vib} = \frac{N k_B \theta_{vib}}{\exp(\theta_{vib}/T) - 1} \quad \text{zero-point energy not included}$$

$$P = N k_B T \left[\frac{\partial (\ln Z)}{\partial \vee} \right]_T$$

for an ideal gas: $P \vee = N k_B T$, $P \bar{v} = R_u T$, $R_u = N_{Avogadro} k_B$

$$S = k_B \ln(W_{tot}) \cong k_B \ln(W_{mp})$$

$$S = N k_B \left[\ln \left(\frac{Z}{N} \right) + T \left(\frac{\partial (\ln Z)}{\partial T} \right)_{\vee} + 1 \right] = N k_B \left[\ln \left(\frac{Z}{N} \right) + 1 \right] + \frac{E}{T}$$

$$\begin{aligned} S_{trans} &= N k_B \left[\ln \left(\frac{Z_{tr}}{N} \right) + T \left(\frac{\partial (\ln Z_{tr})}{\partial T} \right)_{\vee} + 1 \right] = N k_B \left[\ln \left(\frac{Z_{tr}}{N} \right) + 1 \right] + \frac{E_{tr}}{T} \\ &= N k_B \left\{ \frac{5}{2} \ln T - \ln P + \ln \left[\left(\frac{2 \pi m}{h^2} \right)^{3/2} k_B^{5/2} \right] + \frac{5}{2} \right\} \end{aligned}$$

$$S_{int} = N k_B \left[\ln Z_{int} + T \left(\frac{\partial (\ln Z)}{\partial T} \right)_{\vee} \right] = N k_B \ln Z_{int} + \frac{E_{int}}{T}$$

Integrals and Derivatives

$$\int_{x_1}^{x_2} \int_{y_1}^{y_2} f(x) g(y) dx dy = \left[\int_{x_1}^{x_2} f(x) dx \right] \left[\int_{y_1}^{y_2} g(y) dy \right]$$

$$\int_{r_1}^{r_2} \int_{\theta_1}^{\theta_2} \int_{\phi_1}^{\phi_2} f(r) g(\theta) h(\phi) dr d\theta d\phi = \left[\int_{r_1}^{r_2} f(r) dr \right] \left[\int_{\theta_1}^{\theta_2} g(\theta) d\theta \right] \left[\int_{\phi_1}^{\phi_2} h(\phi) d\phi \right]$$

Constants and Conversion Factors

Universal gas constant $R_u = 8.314 \frac{N-m}{(gmol)(K)} = 8.314 \frac{J}{(gmol)(K)} = 8314 \frac{J}{(kmol)(K)}$

Pressure $1 atm = 1.01325 bars = 1.01325 \times 10^5 \frac{N}{m^2} = 0.101325 MPa$

Speed of light $c = 2.998 \times 10^8 \frac{m}{sec} = 2.998 \times 10^{10} \frac{cm}{sec}$

Electron charge $e = 1.602 \times 10^{-19} coul$

Electron mass $m_e = 9.11 \times 10^{-31} kg$

Atomic mass unit $amu = 1.66 \times 10^{-27} kg$

Planck's constant $h = 6.626 \times 10^{-34} J-sec$; $\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34} J-sec$

Dielectric permittivity $\epsilon_0 = 8.854 \times 10^{-12} \frac{coul^2}{J-m}$

Avogadro constant $N_{Av} = 6.022 \times 10^{23} gmol^{-1}$ or $N_{Av} = 6.022 \times 10^{26} kmol^{-1}$

Boltzmann constant $k_B = 1.381 \times 10^{-23} \frac{J}{K}$

$1 J = 1 kg \cdot m^2 / sec^2$

Quadratic solution

For the equation $ax^2 + bx + c = 0$, $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$