Chem 534: Second Exam (100 points total)

Thursday, November 19, 2015

Show all work. Miscellaneous equations and other info is on the back page.

(1) (25 pts) Consider the reaction $CO_2(g) + H_2(g) \Leftrightarrow CO(g) + H_2O(g)$ at 1 bar and 900 K, as well as the following data:

$q_{rot}(H_2) = 5.1397$ $\qquad$ $q_{rot}(CO) = 323.90$ $\qquad$ $\tilde{B}(CO_2) = 0.3902 \text{ cm}^{-1}$

$\tilde{A}(H_2O) = 27.877 \text{ cm}^{-1}$ $\quad$ $\tilde{B}(H_2O) = 14.512 \text{ cm}^{-1}$ $\qquad$ $\tilde{C}(H_2O) = 9.285 \text{ cm}^{-1}$

$\Delta E_r = \Sigma D_e(CO_2) + D_e(H_2) - D_e(CO) - \Sigma D_e(H_2O) = \boxed{-125.1 \text{ kJ/mol}}$ this should have been -29.89 kJ/mol

(a) Calculate the rotational contribution to the equilibrium constant K_c.

$\Theta_r(CO_2) = \dfrac{0.3902}{0.6952} = 0.5613 \text{ K}$ $\qquad$ $q_{rot}(CO_2) = \dfrac{1}{2}\left(\dfrac{900}{0.5613}\right)$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad = 801.71$

$\Theta_A(H_2O) = \dfrac{27.877}{0.6952} = 40.099 \text{ K}$

$\Theta_B = 20.875 \text{ K} \qquad \Theta_C = 13.356 \text{ K}$

$q_{rot}(H_2O) = \dfrac{\pi^{1/2}}{2}\left(\dfrac{900^3}{(40.099)(20.875)(13.356)}\right)^{1/2} = 226.30$

$K_{rot} = \dfrac{(323.90)(226.30)}{(801.71)(5.1397)} = 17.79$

(b) Now compute the electronic contribution.

$q_{elec} = g_{e1}\, e^{\Sigma D_e/kT} = e^{\Sigma D_e/kT}$ $\qquad$ since all singlets.

$K_{elec} = \dfrac{e^{\frac{D_e(CO)}{kT}}\, e^{\Sigma D_e(H_2O)/kT}}{e^{\Sigma D_e(CO_2)/kT}\, e^{D_e(H_2)/kT}}$

$= e^{[D_e(CO) + \Sigma D_e(H_2O) - \Sigma D_e(CO_2) - D_e(H_2)]/kT}$

$= e^{-\Delta E_r/RT} = e^{125.1 \times 10^3/(8.314)(900)} = 1.82 \times 10^7$

(2) (25 pts) Consider again the ClO_2 radical in its $^2B_1$ electronic ground state.

(a) Starting from $S = kT\left(\dfrac{\partial \ln Q}{\partial T}\right)_{N,V} + k\ln Q$, derive the expression for the rotational contribution to the entropy and then calculate it for T=300 K (note: $\Theta_A = 2.489\,\text{K}$, $\Theta_B = 0.481\,\text{K}$, $\Theta_C = 0.403\,\text{K}$)

$Q = \dfrac{q^N}{N!}$ but $N!$ goes w/ translation.

$S_r = NkT\left(\dfrac{\partial \ln q_{rot}}{\partial T}\right)_V + Nk\ln q_{rot}$ $\qquad q_{rot} = \dfrac{\pi^{1/2}}{2}\left(\dfrac{T^3}{\Theta_A \Theta_B \Theta_C}\right)^{1/2}$

$\ln q_{rot} = \ln\left(\pi^{1/2}/2\right) + \tfrac{1}{2}\ln T^3 - \tfrac{1}{2}\ln(\Theta_A\Theta_B\Theta_C)$

$\qquad\quad = \ln\left(\pi^{1/2}/2\right) + \tfrac{3}{2}\ln T - \tfrac{1}{2}\ln(\Theta_A\Theta_B\Theta_C)$

$S_r = \tfrac{3}{2}Nk + Nk\ln\left[\dfrac{\pi^{1/2}}{2}\left(\dfrac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}\right]$

$\quad = (1.5)(8.314) + (8.314)\ln\left[\dfrac{\pi^{1/2}}{2}\left(\dfrac{300^3}{(2.489)(0.481)(0.403)}\right)^{1/2}\right]$

$\quad = 85.6 \text{ J/mol·K}$

(b) Now do the analogous exercise as (a) for the electronic contribution.

$q_{elec} = g_{o1}\,e^{\Sigma D_e/kT}$ $\qquad \ln q_{elec} = \ln g_{e1} + \dfrac{\Sigma D_e}{kT}$

$S_{elec} = NkT\left(-\dfrac{\Sigma D_e}{kT^2}\right) + Nk\left(\ln g_{e1} + \dfrac{\Sigma D_e}{kT}\right)$

$\quad = Nk\ln g_{e1}$

$\quad = (8.314)(\ln 2) = 5.763 \text{ J/mol·K}$

(3) (15 pts) In the high temperature limit, calculate the constant volume molar heat capacity of NH_3 given that the vibrational contribution to $C_{v,m}$ is 2.21 J/mol-K (hint: first obtain an expression for the total energy not including the vibrational contribution)
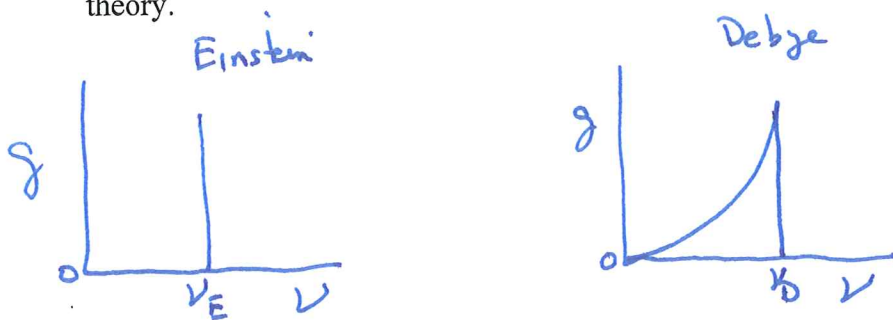
$$E = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right) \quad \text{w/o vibrations} \quad E = \underbrace{\frac{3}{2} NkT}_{(trans)} + \underbrace{\frac{3}{2} NkT}_{(rot)} - \underbrace{N \Sigma D_e}_{(elec)}$$

$$C_v = \left(\frac{\partial E}{\partial T} \right)_V = 3Nk \quad = 3R \quad \text{w/o vibrations}$$

$$C_v = (3)(8.314) + 2.21 = 27.15 \text{ J/mol·K}$$

(4) (20 pts.) Consider a perfect monatomic crystal

(a) Sketch and compare the spectral density function $g(\nu)$ that is used in Einstein theory and the Debye theory.

Einstein: single frequency for all oscillators

Debye: treat acoustic phonons exactly, introduce a cutoff frequency ν_D

(b) Briefly, what was the main drawback of the Einstein treatment? How did the Debye theory overcome these shortcomings? Include a short rationalization on why if works as well as it does. (continue on back if needed)

Einstein treatment led to incorrect behavior of C_v at low T, i.e., it did not yield a T^3 dependence. Debye treated the low frequency modes exactly since these are populated at low T.

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(5) (15 pts.) Consider the classical 2-dimensional harmonic oscillator with Hamiltonian

$$H = \frac{p_x^2 + p_y^2}{2m} + \frac{1}{2}\left(k_x x^2 + k_y y^2\right)$$

(a) Predict the total energy of this system using the equipartition theorem.

$$E = 4\left(\tfrac{1}{2}NkT\right) = 2NkT$$

or $2kT$ for a single molecule

(b) Set up the full expression for the ensemble average of the square of the total momentum, $p^2 = \left(p_x^2 + p_y^2\right)$. Do not solve, but label carefully.

$$\langle p^2 \rangle = \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p^2\, e^{-H/kT}\, dx\, dy\, dp_x\, dp_y}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-H/kT}\, dx\, dy\, dp_x\, dp_y}$$

where $p^2 = p_x^2 + p_y^2$

$$H = \frac{p_x^2 + p_y^2}{2m} + \frac{1}{2}\left(k_x x^2 + k_y y^2\right)$$

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Miscellaneous Information

$k = 1.381 \times 10^{-23}$ J/K $= 0.6952$ cm^{-1}/K

$N_A = 6.022 \times 10^{23}$ mol^{-1} $\qquad R = 8.314$ J mol^{-1} K^{-1}

$h = 6.626 \times 10^{-34}$ J s

$c = 2.9979 \times 10^{10}$ cm/s

1 atm $= 101,325$ Pa $= 1.01325$ bar

$$E = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N} \qquad\qquad S = kT \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k \ln Q \;=\; k \ln Q + \frac{E}{T}$$

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

$$q_{rot} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \qquad \text{or} \qquad q_{rot} = \frac{1}{\sigma} \left(\frac{T}{\Theta_r} \right)$$

$$q_{vib} = \prod_{i=1}^{3n-6(5)} \frac{e^{-\theta_{vi}/2T}}{1 - e^{\theta_{vi}/T}} \qquad\qquad q_{elec} = \sum_i g_{ei} e^{-\varepsilon_i/kT}$$

$$\Theta_r = \frac{hB}{k} = \frac{hc\tilde{B}}{k} \qquad\qquad \Theta_r = \frac{hc\tilde{\nu}}{k}$$

$$\int_{-\infty}^{\infty} e^{-p^2/(2mkT)} \, dp = \sqrt{2\pi mkT}$$

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