Chem. 562
Fall 2009

Name Answer Key

Please put your name on all pages.

Exam 3

Calculators are not allowed for this exam.

You will find that for many questions it is useful to know that $e^{-1} \approx 0.4$ and that other powers can be obtained using $e^{-n} = (e^{-})^n \approx (0.4)^n$.

1. This exam contains 9 pages of questions and instructions, three pages of equations, a page of wavefunctions, a periodic table, and a page of constants and conversion factors.

2. Show your work and make your reasoning clear.

3. You have 2.0 hours to work on the exam.

1.________/20

2.________/25

3.________/15

4.________/20

4.________/20

Total________/100

Answer the following 4 miscellaneous questions about entropy and collision theory.

1a. (5 pts). What is the statistical prediction for the entropy of a perfect crystal at T=0 ? Give a mathematical explanation.

There is only one way to order a crystal, so $W = 1$ and $S = k \ln W = 0$.

1b. (5 pts.) If there are two ways to orient each molecule in the crystal from 0a, how many ways W are there to orient a mole (N_A – Avagardo's number) of such molecules? Use that result to calculate the entropy of the crystal of N_A molecules.

$$W = 2^{N_A}$$

$$S = k \ln 2^{N_A}$$

$$= kN_A \ln 2$$

$$= R \ln 2$$

1c (5 pts). Qualitatively explain how the entropy would be different for a gas of indistinguishable and non-interacting polyatomic versus monatomic molecules.

the rotational entropy would be higher due to the 2nd + 3rd moment of inertia and the additional vibrational modes.

1d. (5 pts.) Consider an elementary bimolecular reaction. If the masses of the gaseous molecules magically increased their masses by a factor of three (such as by forming non-reactive trimers), what does collision theory predict for the change in the rate constant?

$$k_2 = \sigma_c \langle v_{rel} \rangle N_A$$

$$\uparrow$$

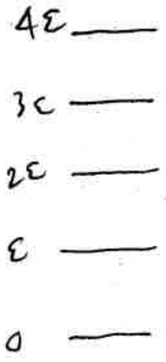
$$\left(\frac{8kT}{\pi\mu}\right)^{1/2}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{3m_1\, 3m_2}{3m_1 + 3m_2} = \frac{9}{3}\mu = 3\mu$$

Rate decreases by $\frac{1}{\sqrt{3}}$

2. To estimate the population of a state, scientists often talk about energy levels in terms of kT. Answer the following questions to learn why.

2a. (5 pts.) Derive the equation for q^v for a harmonic oscillator.



$$q^v = \sum_i e^{-\beta\varepsilon}$$

$$= 1 + \underbrace{e^{-\beta\varepsilon}}_{x} + e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} \ldots$$

$$= 1 + x + x^2 + x^3 \ldots \leftarrow$$

$$= \frac{1}{1-x} = \frac{1}{1-e^{-\beta\varepsilon}}$$

not necessary for exam

$$\Downarrow$$

$$S = 1 + x + x^2 \ldots$$

$$xS = x + x^2 + x^3 \ldots = S - 1$$

$$\therefore 1 = S - xS = S(1-x)$$

$$S = \frac{1}{1-x}$$

2b. (5 pts) Write an expression that gives the percent population of the eigenstate ε_i for a harmonic oscillator.

$$P_i = \frac{n_i}{q^v} = \frac{e^{-\beta\varepsilon_i}}{\frac{1}{1-e^{-\beta\varepsilon}}} = e^{-\beta\varepsilon_i}(1-e^{-\beta\varepsilon})$$

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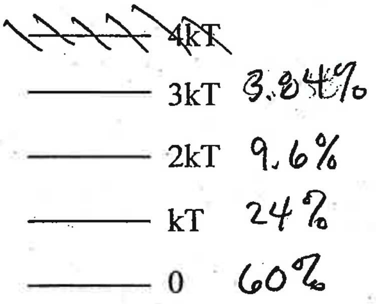
2c. (10 pts) Consider a harmonic oscillator that has an energy level spacing of kT. For each eigenstate drawn below, label its population. In %.



$g = (1-e^{-\beta\varepsilon})$

$= (1-e^{-\varepsilon/kT})$

$= (1-e^{-1})$

$= 1-0.4$

$= 0.6$

$P_0 = e^{0} \cdot 0.6 = 0.6$

$P_1 = e^{-1} \cdot 0.6 = 0.4 \cdot 0.6$

$= 0.24$

$P_2 = e^{-2} \cdot 0.6 = (e^{-1})^2\, 0.6$

$= 0.4 \cdot 0.4 \cdot 0.6$

$= 0.096$

$P_3 = e^{-3} \cdot 0.6 = (0.4)^3 \cdot 0.6$

$= 0.096 \times 0.4$

$= 0.0384$

0.4
( )

2d. (5 pts) In lecture, we found that I_2, which has a frequency of $\tilde{\upsilon} = 215\ \text{cm}^{-1}$, has 23% of its population in the $\upsilon=1$ level and that Cl_2, which has a frequency of $\tilde{\upsilon} = 560\ \text{cm}^{-1}$, has 6% of its population in the $\upsilon=1$ level. Using your results above, what is the approximate population of $\upsilon=1$ for BrI, which has a frequency of $\tilde{\upsilon} = 410\ \text{cm}^{-1}$? Show your work.

xact BrI $\nu \approx 420$
$\approx 2kT$

$g = (1-e^{-2})$

$= (1-0.4 \cdot 0.4)$

≈ 0.8

$P_1 = e^{-2} \cdot 0.8$

$\approx 0.16 \times 0.8$

$\approx 0.2 \times 0.8$

≈ 0.16

$\approx 16\%$

Notice from I_2 & Cl_2 that population can be estimated by comparing to kT.

e.g. $I_2 = 215\ \text{cm}^{-1} \approx kT$ from above $P_1 = 24\%$

versus 23% in class.

Cl_2 is not quite 3kT : from above $P_3 = 3.8\%$.

$\therefore$ for BrI ~ ~~40~~ $410\ \text{cm}^{-1} \simeq 2kT$; estimate $P = 10\%$.

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Answer the following 2-part question to learn about the density of the atmosphere.

3a. (5 pts.) Write the expression for the ratio of the number of molecules in a state with energy ε_1 to the number in a state with energy ε_0 at a temperature T.

$$P_{\varepsilon_1} = \frac{n_1}{q} = \frac{e^{-\beta\varepsilon_1}}{q} \qquad \frac{P_{\varepsilon_1}}{P_{\varepsilon_0}} = \frac{e^{-\beta\varepsilon_1}}{e^{-\beta\varepsilon_0}} = e^{-\beta(\varepsilon_1-\varepsilon_0)}$$

$$P_{\varepsilon_0} = \frac{n_0}{q} = \frac{e^{-\beta\varepsilon_0}}{q}$$

3b. (10 pts.) The energy of a particle in a gravitational field is $\varepsilon = mgh$ where m is the mass of the particle, h is the height above a reference point, and $g \approx 10$ m/s2 is the acceleration of gravity. Estimate the ratio of the number density of O_2 at 8314 m compared to that at sea level. Assume that the temperature is 320 K.

$$e^{-\beta(\varepsilon_1-\varepsilon_0)} = \exp\left[-\frac{32\,g/mole\cdot\frac{kg}{1000\,g}\times\frac{10\,m}{s^2}\,(8314\,m - 0\,m)}{\frac{8.314\,J}{mol\,K}\cdot 320\,K}\right]$$

10

$$= \exp\left[-10^{-1}\times 10^{-3}\times 10\times 10^{3}\right] = \exp[-1] = 0.4$$

$$\frac{P_{\varepsilon_1}}{P_{\varepsilon_0}} = e^{-1} = 0.4$$

so, pressure of O_2 at 8314 m is about 40% of that at sea level.

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4a. (5 pts.) Derive the equation for the equilibrium constant K for the chemical reaction A ↔ B, where the eigenstates of A and B are spaced by ε_A and ε_B, respectively, and the relative energy of B is offset by $\Delta\varepsilon_{AB}$. Start from the definition of K = [B]/[A].

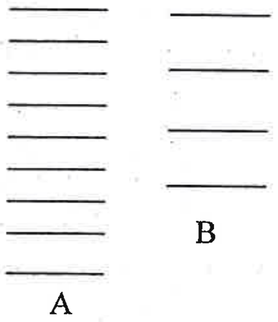
$$K = \frac{[B]}{[A]} = \frac{N_B}{N_A} \longleftarrow \text{fraction in B}$$

$$\text{fraction in A: } \frac{\#\text{ in A}}{\text{total}} = \frac{\sum_j e^{-\beta\varepsilon_{JA}}}{q} = \frac{q_A}{q}$$

$$\frac{\#\text{ in B}}{\text{total}} = \frac{e^{-\beta\Delta\varepsilon_{AB}} \sum_k e^{-\beta\varepsilon_{kB}}}{q} = \frac{q_B}{q}$$

$$K = \frac{N_B}{N_A} = \frac{q_B}{q_A} e^{-\beta\Delta\varepsilon_{AB}} = \frac{\sum_k e^{-\beta\varepsilon_{kC}}}{\sum_j e^{-\beta\varepsilon_{JA}}} e^{-\beta\Delta\varepsilon_0}$$

4b. (5 pts) If the eigenstates have the relative spacings drawn below, explain whether the equilibrium constant will favor A or B and <u>why</u>.



Will favor A because of the more closely spaced eigenstates <u>and</u> because of the lower ground state.

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4c. (5 pts) Calculate K for $\varepsilon_A = kT$, $\varepsilon_B = 2kT$ and $\Delta\varepsilon_{AB} = 2\ kT$ for vibrational mode in the high temperature limit. Round your answer to 1 significant digit.

high temp limit doesn't alter question

ok without

$$K = \frac{q_B}{q_A} e^{-\beta\Delta\varepsilon_{AB}} = \frac{(1-e^{-\beta\varepsilon_A})}{(1-e^{-\beta\varepsilon_B})} e^{-\beta\Delta\varepsilon_{AB}}$$

$$= \frac{(1-e^{-1})}{(1-e^{-2})} e^{-2}$$

$$= \frac{(1-0.4)}{(1-0.16)} 0.16$$

$$= \frac{0.6}{0.84} \cdot 0.16 \approx \frac{0.6}{0.8} \times 0.2 = \frac{0.6}{4} \approx 0.15$$

w/ high temp limit, could taylor expand $1-e^{-\beta\varepsilon} = 1-1-\beta\varepsilon \ldots$

$$\frac{\varepsilon_A}{\varepsilon_B} \cdot e^{-\beta\Delta\varepsilon_{AB}} = \frac{1}{2} \cdot 0.16$$

$$= 0.08 \approx 0.1$$

4d. (5 pts) To make K = 1, what value would $\Delta\varepsilon_{AB}$ need to be? Write an expression (do not evaluate).

$$1 = \frac{q_B}{q_A} e^{-\beta\Delta\varepsilon_0}$$

$$e^{-\beta\Delta\varepsilon_0} = \frac{q_A}{q_B}$$

$$-\beta\Delta\varepsilon_0 = \ln q_A/q_B$$

$$\Delta\varepsilon_0 = +\frac{1}{\beta}\ln\frac{q_B}{q_A}$$

5a. (5 pts) Write out the equation for the canonical partition function Q in terms of the molecular translational, rotational, and vibrational partition functions (e.g. q^T, q^R, q^V) for a <u>homo</u>nuclear diatomic gas in the high temperature limit.

$$q = q_T q_R q_V \qquad Q = \frac{q^N}{N!} = \frac{(q_T q_R q_V)^N}{N!}$$

from the ~~ba~~ eqn page

$$Q = \frac{1}{N!}\left[\frac{V}{\Lambda^3} \times \frac{1}{\sigma}\frac{kT}{hcB} \times \frac{1}{(1-e^{-hc\tilde{\nu}/kT})}\right]^N$$

5b. (5 pts.) Find the equation for $<E^T>$ for the homonuclear diatomic gas.

$$q^T = q_x^T q_y^T q_z^T = \frac{V}{\Lambda} = \frac{V}{\beta^{1/2}(\ldots)}$$

$\nearrow$

$$\Lambda = \left(\frac{h^2\beta}{2\pi m}\right)^{1/2} = \beta^{1/2}(\ldots)$$

$$\langle E^T \rangle = -\left(\frac{\partial \ln \beta^{-3/2}}{\partial \beta}\right)_V = +\frac{3}{2}\left(\frac{\partial \ln \beta}{\partial \beta}\right)_V$$

$$= \frac{3}{2}\frac{1}{\beta}$$

$$= \frac{3}{2}kT$$

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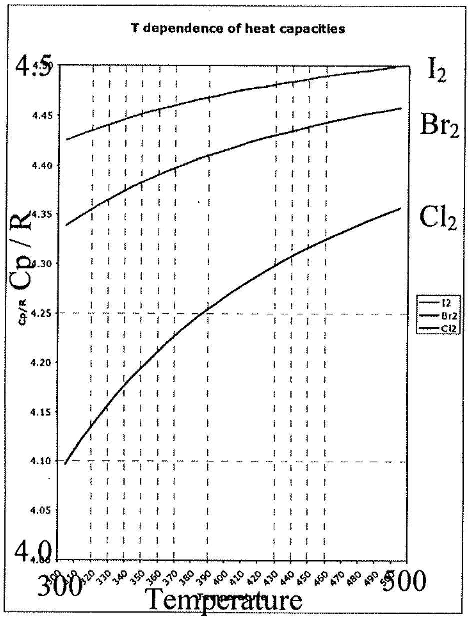
5d. (10 pts) Shown below is Cp measured as a function of T for Cl_2, Br_2 and I_2. Answer the following questions, assuming that the gases are non-interacting. As a reminder, Cp = Cv + R, and that $Cv = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_V$.

1. What values of Cp should Cl_2, Br_2 and I_2 reach as the temperature is raised?
2. At T = 300 K, why does Cl_2 have a much lower value of Cp than I_2?
3. What value would you expect Cp to reach at high T for a linear triatomic like HCN? Explain.



1) At the high-temp limit, all modes store energy equally, so they all approach $\frac{9}{2}R$

2) The Cl-Cl bond is much higher in frequency, so the available thermal energy cannot be stored as readily in the vibrational degree of freedom.

3) Each vibrational mode stores R, and there are 3N-5 = 4 vib modes in the linear HCN molecule

$$Cp = \underset{\text{Trans}}{\frac{3}{2}R} + \underset{\text{rot}}{R} + \underset{\text{vib}}{4R} + \underset{\overset{\uparrow}{Cp = Cv + R}}{R_9} = 7.5R$$