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

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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.

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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?

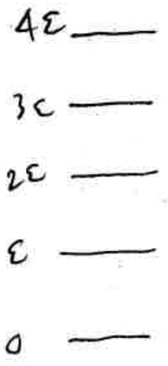
$$k_2 = \sigma_c \underset{\uparrow \atop \left(\frac{8kT}{\pi\mu}\right)^{1/2}}{\langle v_{rel} \rangle} N_A$$

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

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.



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

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

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

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

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.

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

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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 %.

~~4kT~~
3kT 3.84%
2kT 9.6%
kT 24%
0 60%

$$q = (1-e^{-\beta\varepsilon}) = (1-e^{-\varepsilon/kT}) = (1-e^{-1}) = 1-0.4 = 0.6$$

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

$$P_1 = e^{-1}\cdot 0.6 = 0.4\cdot 0.6 = 0.24$$

$$P_2 = e^{-2}\cdot 0.6 = (e^{-1})^2\, 0.6 = 0.4\cdot 0.4\cdot 0.6 = 0.096$$

$$P_3 = e^{-3}\cdot 0.6 = (0.4)^3\cdot 0.6 = 0.096\times 0.4 = 0.0384$$

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.

Exact BrI $\nu = 420 \approx 2kT$

$q = (1-e^{-2}) = (1-0.4\cdot 0.4) \approx 0.8$

$P_1 = e^{-2}\cdot 0.8 \approx 0.16\times 0.8 \approx 0.2\times 0.8 \approx 0.16 \approx 16\%$

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 $P_3 = 3.8\%$.

∴ for BrI ~ ~~40~~ 410 cm⁻¹ ≃ 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.

4a. (5 pts.) Derive the equation for the equilibrium constant K for the chemical reaction $A \leftrightarrow B$, 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].

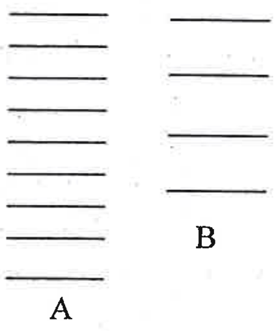
$$K = \frac{[B]}{[A]} = \frac{N_B}{N_A} \longleftarrow \text{fraction in B}$$

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

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

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

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



Will favor A because of the more closely spaced eigenstates and 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.

ok without

high temp limit doesn't alter question

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

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

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

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

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 ~~bx~~ eqn page

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

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

$$q^T = q^T_x q^T_y q^T_z = \frac{V}{\Lambda} = \frac{V}{\beta^{1/2}(\ldots)}$$

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

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

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

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