Chem. 562
Spring 2012

Name Key

Please put your name on all pages.

Exam 3

Calculators are not allowed for this exam.

Especially useful facts:

Powers of exponentials can be obtained using $e^{-xn} = (e^{-x})^n$.

$e^{-1} \approx 0.4$

$e^{-0.5} \approx 0.6$

Multiples of logs can be done with $\ln(x^n)=\sum_n \ln(x)$, such as $\ln(x^2)=\ln(x)+\ln(x)$.

$\ln(2)\approx 0.7$

$kT \approx 200\ \mathrm{cm}^{-1}$ at room temperature, because $k=1.38\times10^{-23}$ J/K $\approx 0.7\ \mathrm{cm}^{-1}/\mathrm{K}$.

1. This exam contains 10 pages of questions and instructions and 3 pages of equations and integrals.
2. Show your work and make your reasoning clear.
3. You have 1.5 hours to work on the exam.

1.________/15

2.________/20

3.________/15

4.________/30

5.________/25

Total ______/100

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1. Answer these questions about ideal gases.

1a. (5 pts). Given that $q^R \approx 2$ ~~cm~~$^{-1}$ for H_2 at very high temperatures, what is q^R for D_2 ?

$$q^R = \frac{kT}{hc}\frac{1}{B} \qquad B = \frac{\hbar^2}{2\mu R^2 hc} \qquad \therefore\ q^R \propto \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\frac{q_{D_2}}{q_{H_2}} \propto \frac{\mu_{D_2}}{\mu_{H_2}} = \frac{\frac{2\cdot 2}{2+2}}{\frac{1\cdot 1}{1+1}} = \frac{1}{\frac{1}{2}} = 2 \qquad \therefore\ q_{D_2} = 4\ \text{cm}^{-1}$$

1b. (5 pts) The rotational constant of the OH radical is about 100 cm^{-1}. Calculate the relative populations of the first three rotational states, e.g. $P_{J=0} : P_{J=1} : P_{J=2}$, at room temperature.

Do not need q, because relative is asked.

terms: $g(J)e^{-\beta E_J} \propto (2J+1)e^{-\beta J(J+1)}$

$J=0 \qquad e^0 = 1$

$J=1 \qquad 3e^{-2B/kT} = 3e^{-200\,\text{cm}^{-1}/200\,\text{cm}^{-1}} = 3e^{-1} = 3\cdot 0.4 = 1.2$

$J=2 \qquad 5e^{-6B/kT} = 5e^{-3} = 5\cdot(0.4)^3 = 5\cdot 0.16\cdot 0.4$
$= 2\cdot 0.16$
$= 0.32$

$\boxed{1 : 1.2 : 0.32}$

1c. (5 pts). Derive pV=nRT for a monotonic ideal gas.

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T \qquad q = \left(\frac{2\pi M}{\beta h^2}\right)^{3/2} V \qquad \ln q = \ln V + \frac{3}{2}(\ldots)$$

$$Q = \frac{q^N}{N!}\ ; \quad \ln Q = N\ln q - \ln N!$$

$$= NkT\left(\frac{\partial \ln q}{\partial V}\right)_T = NkT\,\underbrace{\frac{d}{dV}\bigl(\ln V}_{1/V} + \frac{3}{2}(\ldots)\bigr)$$

$$= \underbrace{Nk}_{R}T\,\frac{1}{V}$$

$$= NR\frac{1}{V}$$

2. A group of amateur astronomers want to estimate the temperature of a star using statistical mechanics and spectroscopy. They assume that the star is composed entirely of hydrogen. Recall that the electronic energy levels of a hydrogen atom are given by

$$E_n = -13.6eV\frac{1}{n^2} \approx -10^5 cm^{-1}\frac{1}{n^2}$$

2a. (5 pts). Draw an energy diagram (an energy level ladder) for the lowest three electronic states of the hydrogen atom and label them with the appropriate energies in cm^{-1}. Use fractions.

——— $n=3$ $E_3 = -\frac{1}{9}\cdot 10^5\ cm^{-1}$

——— $n=2$ $E_2 = -\frac{1}{4}\cdot 10^5\ cm^{-1}$

——— $n=1$ $E_1 = -10^5\ cm^{-1}$

2b. (5 pts). Redraw your diagram with the energies of your levels shifted such that the ground state has a relative energy of zero.

add $1\times10^5\ cm^{-1}$ to each.

$E_3 = \left(-\frac{1}{9}+1\right)\times 10^5\ cm^{-1} = \frac{8}{9}\times 10^5\ cm^{-1}$

——— $n=3$

——— $n=2$ $E_2 = \left(-\frac{1}{4}+1\right)\times 10^5\ cm^{-1} = \frac{3}{4}\times 10^5\ cm^{-1}$

——— $n=1$ $E_1 = 0$

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2c. (5 pts). Assuming that only these three states are relevant, calculate the electronic partition function at T=5778 K, which is the surface temperature of our sun. Show your work. Round your answer to 2 significant figures.

$$q = \sum_i e^{-\beta \varepsilon_i}$$

$$= e^{0} + \underbrace{e^{-\frac{0.75\times 10^{5}\ \text{cm}^{-1}}{5778\text{k} \times 0.7\ \text{cm}^{-1}/\text{K}}}}_{\approx e^{-10^{3}} \simeq 0} + \underbrace{e^{-\frac{8}{9}\times 10^{5}\ \text{cm}^{-1}/5778\text{k}\times 0.7\ \text{cm}^{-1}/\text{K}}}_{\approx 0}$$

$$= 1.0$$

2d. (5 pts). For an unknown star, the ratio of the populations of the ground and first electronic excited states of hydrogen is $\frac{P_{i=0}}{P_{i=1}} = 8.0$. Calculate the temperature of the unknown star to 1 significant figure.

$$\frac{P_{i=0}}{P_{i=1}} = \frac{\frac{e^{-\beta \varepsilon_{i=0}}}{\cancel{q}}}{\frac{e^{-\beta \varepsilon_{i=1}}}{\cancel{q}}} = \frac{e^{-\beta \varepsilon_{i=0}}}{e^{-\beta \varepsilon_{i=1}}} = \frac{1}{e^{-\varepsilon_{i=1}/kT}} = e^{+\varepsilon_{i=1}/kT} = 8$$

$$\frac{\varepsilon_{i=1}}{kT} = \ln 8$$

[illegible] 100000

$$T = \frac{\varepsilon_{i=1}}{\ln(8)\cdot k} = \frac{\cancel{0.7}5\times 10^{5}\ \text{cm}^{-1}}{(\ln(2)+\ln(2)+\ln(2))\cdot \cancel{0.7}\ \text{cm}^{-1}/\text{K}} = \frac{1}{2}\times 10^{5}\ \text{K}$$

$0.7 + 0.7 + 0.7$

$= 2.1$

$= 50{,}000$ K.

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3. For particles that are noninteracting and indistinguishable, the Sackur-Tetrode equation give the entropy S of a monatomic ideal gas

$$S = nR\ln\left(\frac{e^{5/2}V}{N\Lambda^3}\right) = nR\ln\left(\frac{e^{5/2}V}{nN_{AV}\Lambda^3}\right)$$

where V is the volume of the container, n is the number of moles of particles, N_{AV} is Avagadro's number and Λ is the thermal wavelength.

The following questions about this equation are independent of each other. You do not have to do the first part to do the other parts.

3a. (5 pts.) Starting with the expression for entropy in the canonical ensemble, derive the Sackur-Tetrode equation by substituting the translational partition function. In the derivation, Sterling's Approximation will be useful. Also, remember that $\frac{5}{2} = \ln e^{5/2}$ and that we proved $U - U(0) = \frac{3}{2}nRT$ for an ideal gas.

2 $$S = \frac{U - U(0)}{T} + k\ln Q \qquad Q = \frac{q^N}{N!}$$

2

$$= \frac{\frac{3}{2}nRT}{T} + k\ln\frac{q^N}{N!} = \frac{3}{2}nR + k\left(N\ln q - \underbrace{\ln N!}_{N\ln N - N}\right)$$ 4

$$= \frac{3}{2}nR + kN\ln q - kN\ln N - kN$$

$$= \frac{3}{2}nR + n\underbrace{kN_{AV}}_{R}\ln q - n\underbrace{kN_{av}}_{R}\ln N - n\underbrace{kN_{AV}}_{R}$$

$$= \frac{5}{2}nR + nR(\ln q - \ln N)$$

$$= \frac{5}{2}nR + nR\ln\frac{q}{N} \qquad \text{but } q = \frac{V}{\Lambda^3}$$

$$= nR\ln e^{5/2} + nR\ln\frac{V}{N\Lambda^3} \qquad nN_{AV}$$

$$S = nR\ln\left(\frac{e^{5/2}V}{nN_A\Lambda^3}\right)$$

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3b. (5 pts.) Use the Sackur-Tetrode equation to write an expression for the entropy change ΔS upon expanding a monatonic gas from a volume V_i to a final volume V_f at constant temperature. Explain the physical origin of the change in entropy.

$$\Delta S = S_f - S_i = nR\ln(aV_f) - nR\ln(aV_i)$$

all the constants

$$= nR\left[\ln(aV_f) - \ln(aV_i)\right]$$

$$= nR\ln\left(\frac{V_f}{V_i}\right)$$

3c. (5 pts). Explain how the entropy, S, would be different for a gas of indistinguishable and noninteracting polyatomic molecules. Explain how the entropy change, ΔS, for an expansion of this polyatomic gas would different from that of the monatomic gas.

The entropy would be.... larger because there are additional vibrational + rotational degrees of freedom.

The entropy change would be... the same, because the volume change does not alter the rotational or vibrational degrees of freedom.

4. Consider the ion-molecule reaction of $X + X^- \leftrightarrow X_2^-$. There is an energy offset of $\Delta\varepsilon_0$ between the reactants and products.

4a. (5 pts). Starting from z=collisions/Δt, derive an expression for the average collision rate $\langle Z_{AB}(v_{rel})\rangle$ as a function of $[X]$ and $[X^-]$, assuming that every collision leads to products and that the cross section is independent of the translational velocities.

$$z = \frac{\text{collisions}}{\Delta t} = \frac{\text{Vol.}\; N_B}{\Delta t} = \frac{\sigma_c V_{rel} \cancel{\Delta t} N_B}{\cancel{\Delta t}} = \sigma_c V_{rel} N_B$$

$$Z_{AB}(v_{rel}) = \sigma_c v_{rel} N_A N_B$$

$$\langle Z_{AB}(v_{rel})\rangle = \int \sigma_c v_{rel} N_A N_B f(v_{rel})\, dv_{rel}$$

$$= \sigma_c N_A N_B \langle v_{rel}\rangle \qquad N_A = N_{AV}[A]$$

$$N_B = N_{AV}[B]$$

$$= \sigma_c \langle v_{rel}\rangle N_{AV}^2 [A][B]$$

$$\Rightarrow \langle Z_{X X^-}\rangle = \sigma_c \langle v_{rel}\rangle N_{AV}^2 [X][X^-]$$

4b. (5 pts.) Write down the partition function q_X for the reactants in a large container of volume V.

$$q_{X^-}^T = q_X^T = \frac{V}{\Lambda^3} \quad \text{because only translations.}$$

4c. (5 pts). Write down the partition function q_{X2} for X_2 applicable to any temperature.

$$q_{X^2} = q^T q_v q_R = \frac{V}{\Lambda^3}\left[\sum_J (2J+1) e^{-hc\beta J(J+1)}\right] \frac{1}{1 - e^{-\beta hc\tilde{\nu}}}$$

4d. (5 pts.) Write an expression for the equilibrium constant K in terms of q_X and q_{X2}.

$$k = \frac{[X_2]}{[X][X^-]} = \frac{q_{X^2}}{q_X^2} e^{-\Delta\varepsilon_0\beta}$$

4e. (5 pts). If $q_X = q_{X2} = 2$ and $\Delta\varepsilon_0 = -500\text{ cm}^{-1}$, what temperature would be needed to make it a reactant favored reaction?

$$\frac{2}{4} e^{-\Delta\varepsilon_0\beta} = 1$$

must be smaller than 1 to be reactant favored

$$-\Delta\varepsilon_0\beta = \ln(2)$$

$$-\frac{\Delta\varepsilon_0}{k\ln 2} = T = \frac{-(-500\text{ cm}^{-1})}{0.7\text{ cm}^{-1}/k \cdot 0.7} = \frac{500}{0.48}\,K \approx 1000\,K.$$

4f. (5 pts.) The collisional cross section of ion-molecule reactions are typically larger than the sum of the radii e.g. $\sigma_c > \pi\left(\frac{R_X + R_{X-}}{2}\right)^2$, especially when the neutral atom is very electronegative. Provide a 1 sentence hypothesis for why that is true.

Ion-molecule rxn do not act as hard spheres because an e^- transfer occurs before a hard collision.

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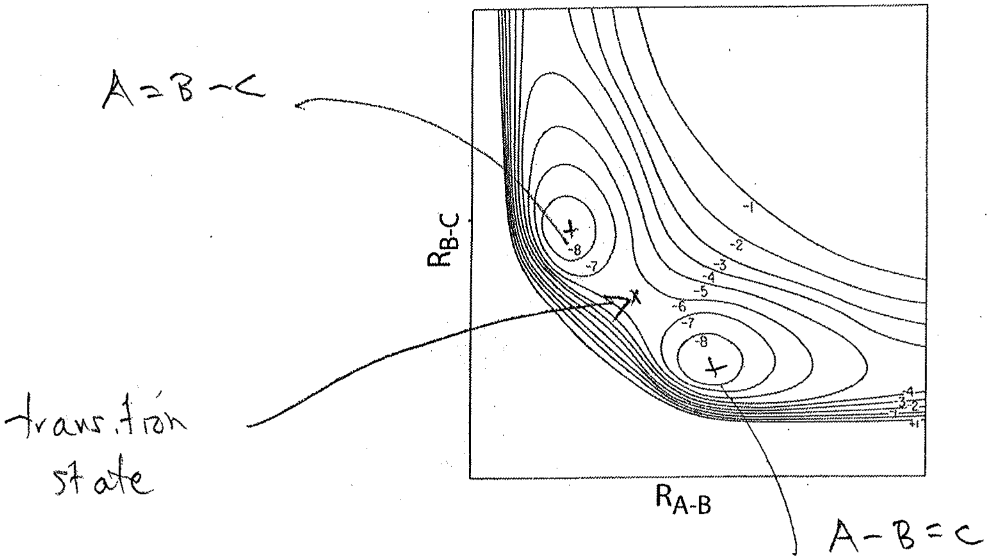
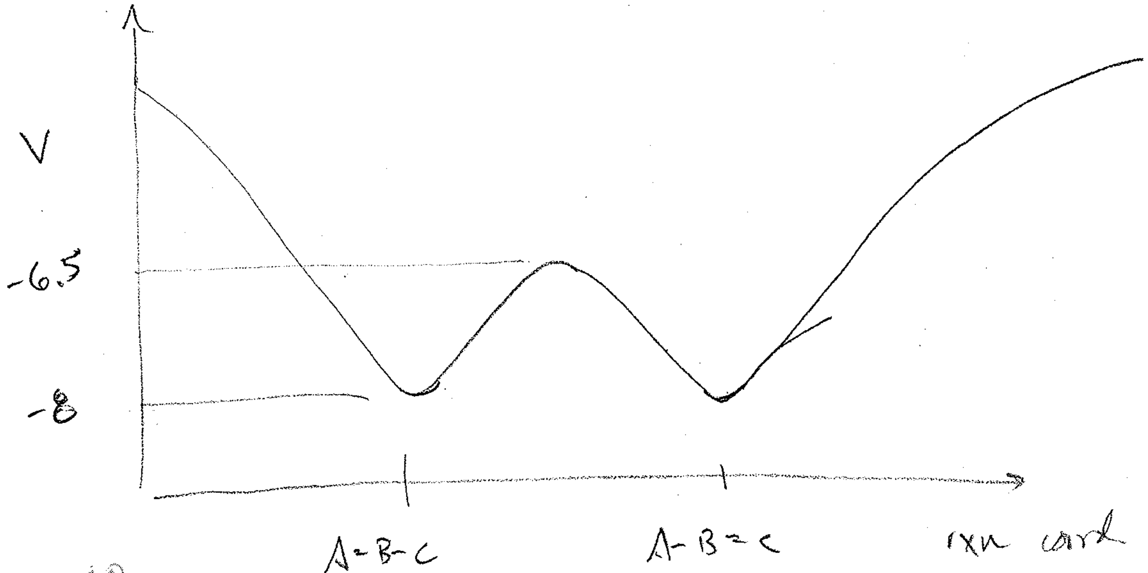
5. Consider the equilibrium between the isomers A-B=C ↔ A=B-C.

5a. (5 pts). On the 2D potential energy surface below, mark the location of the two isomers and the location of the transition state.



5b. (5 pts) Draw the reaction coordinate for the isomerization. Make sure that your y-axis units accurately reflects the potential energy of the reaction.



9
3
12

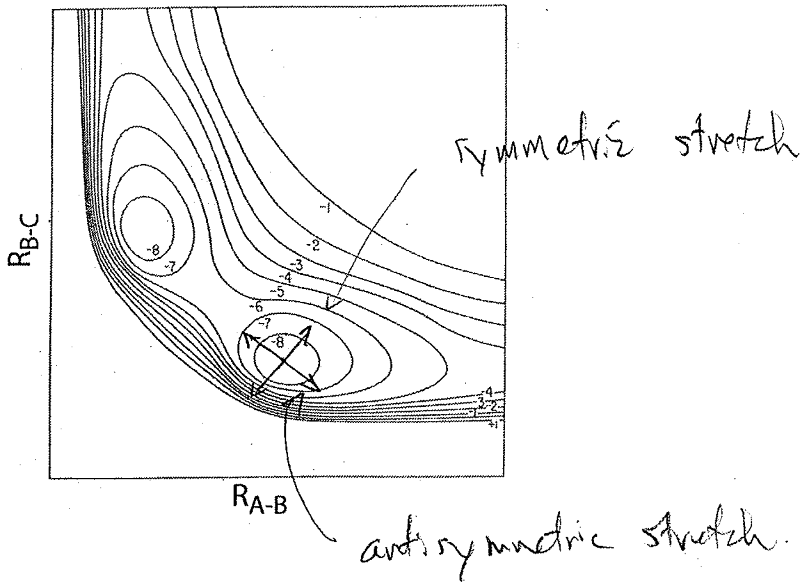
10
3
13

10
6
16

~~10~~ 9
3

19

5c. (5 pts) In the potential energy surface below, draw and label lines indicating the symmetric and antisymmetric stretch normal mode coordinates of the A-B=C isomer.



5d. (5 pts) If you could selectively impart vibrational energy into the molecule, would you excite the symmetric, antisymmetric or bending mode of A-B=C to promote isomerization. Explain in 1 sentence.

antisymmetric, because that is the vibrational coordinate that points along the reaction coordinate to the opposite isomer