

Columbia University in the City of New York
New York, N.Y. 10027

Chemistry C2407x
First Exam
October 1, 1998

Total Points: 150

1998
George Flynn
75 Minutes

Answer Key

All questions are NOT weighted equally. I have attempted to order the questions from the least difficult to the most difficult, but "beauty is in the eye of the beholder", so skip around to find the problems that are easiest for you. Good luck!

Please print your name in the boxes provided and sign where indicated. Tear off this sheet and pass it to the right for the proctors to pick up.

Print your last name:

Print your first name:

Signature: _____

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Do not write anything else on this page. Answer the questions in the spaces provided on the following pages.

1a

3a

1b

3b

1c

2a

4a

2b

4b

2c

4c

4d

4e

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Problem 1: (40 points) [Oxtoby Problem 7.17] A sample of 0.500 moles of neon gas, initially at 1.00 atm. and 273 K, expands against a constant external pressure of 0.1 atm until the gas pressure reaches 0.2 atm and the temperature reaches 210 K.

a) (20 points) Calculate the work done on the gas. Show all reasoning clearly.

$$w = -p \Delta V = -p(V_f - V_i)$$

p given as 0.1 atm

$$V_i = nRT_i / p_i \quad V_f = nRT_f / p_f$$

$$w = -pnR(T_f / p_f - T_i / p_i)$$

$$T_f = 210 \text{ K} \quad T_i = 273 \text{ K}$$

$$p_f = 0.2 \text{ atm} \quad p_i = 1.00 \text{ atm}$$

$$w = -nR (210 \text{ deg} (0.1/0.2) - 273 \text{ deg} (0.1/1.00))$$

$$w = -nR (105 - 27.3)$$

$$w = -(0.5 \text{ moles})(8.314 \text{ joules/mole-deg})(77.7 \text{ deg})$$

$$w = -323 \text{ joules}$$

b) (10 points) Calculate the change in the internal energy of the neon gas. Show all reasoning clearly.

$$E = \frac{3}{2} nRT$$

$$E = E_f - E_i$$

$$E = \frac{3}{2} nR(T_f - T_i)$$

$$n = 0.5 \text{ moles}, T_f = 210 \text{ deg}, T_i = 273 \text{ deg} \text{ (all given)}$$

$$E = (\frac{3}{2})(0.5)(8.314)(210 - 273) \text{ joules}$$

$$E = -392.8 \text{ joules}$$

c) (10 points) Calculate the heat absorbed by the gas in this expansion. Show all reasoning clearly.

$$E = q + w$$

$$q = E - w$$

$$E = -392.8 \text{ joules (part b)}$$

$$w = -323 \text{ joules (part a)}$$

$$q = -392.8 - (-323) \text{ joules}$$

$$q = -69.8 \text{ joules}$$

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Problem 2: (40 Points) [Much in common with Oxtoby problems 4.41-4.43, 13.44, 13.45] A mixture of NO ($M=0.030$ Kg/mole) and O_2 ($M=0.032$ Kg/mole) is prepared such that the partial pressure of each gas is just 1 atm. You are reminded that the ideal gas law for such a system can be written:

$$P_i V = n_i RT$$

where n_i , the number of moles of species i , is $n_i = N_i / N_0$. N_0 is Avagadro's number and N_i the total number of molecules of species i in the volume V . At 200 K the reaction between NO and O_2 can be ignored. You may treat the gases as ideal and use the binary collision model to treat NO/ O_2 collisions. This is very much a numerical problem. Be very careful with the "routine" calculations. You may find the following information useful:

$\mu = m_a m_b / (m_a + m_b)$ and $N_0 \mu = M_a M_b / (M_a + M_b)$, where N_0 is Avagadro's number, m_i is a molecular mass and M_i is the molecular weight of species i .

R (the gas constant) = $8.2 \times 10^{-5} \text{ m}^3 \text{-atm/mole-deg} = 8.314 \text{ joules/mole-deg}$

a) (15 points) Compute the relative mean speed $\langle u_{\text{rel}} \rangle$ of O_2 with respect to NO. Show all reasoning and calculations clearly and be especially careful about units!

$$\langle u_{\text{rel}} \rangle = (8 kT / \mu)^{1/2} \text{ Free formula}$$

$$\langle u_{\text{rel}} \rangle = (8(N_0 k)T / (N_0 \mu))^{1/2}$$

$$\langle u_{\text{rel}} \rangle = (8RT / (N_0 \mu))^{1/2}$$

$$N_0 \mu = M_{\text{NO}} M_{\text{O}_2} / (M_{\text{NO}} + M_{\text{O}_2}) \text{ (given)}$$

$$N_0 \mu = [(0.030)(0.032) / (0.030 + 0.032)] \text{ kg/mole}$$

$$N_0 \mu = 0.0155 \text{ kg / mole}$$

$$\langle u_{\text{rel}} \rangle = ((8)(8.314)(200) / (0.0155))^{1/2} \text{ meter/s}$$

$$\langle u_{\text{rel}} \rangle = 522.7 \text{ m/s}$$

b) (15 points) Compute the number of NO molecules per m^3 and the number of O_2 molecules per m^3 for this sample. Show your work clearly.

$$P_i V = n_i RT = (N_i / N_0) RT \quad \text{given}$$

$$(N_i / V) = P_i (N_0 / RT)$$

$$P_{\text{NO}} = P_{\text{O}_2} \quad \text{given (both = 1 atm)}$$

Print your name here:

$$N_{\text{NO}}/V = N_{\text{O}_2}/V$$

$$N_{\text{NO}}/V = \frac{(1 \text{ atm})(6.023 \times 10^{23} \text{ molecules/mole})}{(8.2 \times 10^{-5} \text{ m}^3\text{-atm/mole-deg})(200 \text{ deg})}$$

$$(R = 8.2 \times 10^{-5} \text{ m}^3\text{-atm/mole-deg} \quad \text{given})$$

$$N_{\text{NO}} / V = 3.67 \times 10^{25} \text{ molecules/m}^3$$

$$N_{\text{O}_2} / V = 3.67 \times 10^{25} \text{ molecules/m}^3$$

c) (10 points) If the radius of both NO and O₂ molecules is 2.0x10⁻¹⁰ meter, compute the total gas kinetic collision rate per m³, Z_{AB}, for all NO colliding with all O₂. Show your work clearly.

$$Z_{\text{AB}} = \frac{1}{2} \langle u_{\text{rel}} \rangle^2 (N_{\text{A}}/V) (N_{\text{B}}/V) \quad \text{Free formula}$$

$$r_{\text{AB}} = 2.0 \times 10^{-10} \text{ m} + 2.0 \times 10^{-10} \text{ m} = 4.0 \times 10^{-10} \text{ meter}$$

$$\langle u_{\text{rel}} \rangle = 523 \text{ m/s} \quad (\text{part a})$$

$$N_{\text{A}}/V = N_{\text{B}}/V = 3.67 \times 10^{25} \text{ molecules/m}^3 \quad (\text{part b})$$

$$Z_{\text{AB}} = (4 \times 10^{-10} \text{ m})^2 (523 \text{ m/s}) (3.67 \times 10^{25} \text{ molecules/m}^3)^2$$

$$Z_{\text{AB}} = (16 \times 10^{-20}) (523) (1.35 \times 10^{51}) (\text{m}^2/\text{molecule}) (\text{m/s}) (\text{molecules/m}^6)$$

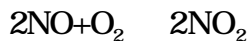
$$Z_{\text{AB}} = 3.54 \times 10^{35} \text{ molecules/m}^3\text{-s}$$

$$\text{Optional } 1 \text{ m}^3 = (10^2 \text{ cm})^3 = 10^6 \text{ cm}^3 = 10^3 \text{ liters}$$

$$Z_{\text{AB}} = 3.54 \times 10^{35} \frac{\text{molecules}}{\text{m}^3\text{-s}} \times \frac{1 \text{ m}^3}{10^3 \text{ liters}}$$

$$Z_{\text{AB}} = 3.54 \times 10^{32} \text{ molecules/l-sec.}$$

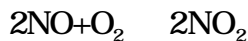
Problem 3: (30 points) When the temperature of the mixture in problem 2 is raised to 300K, reaction between NO and O₂ occurs:



At 300 K the reaction rate R is observed to be equal to 10⁻⁷ Z_{AB} while at 330 K, R is observed to be 3x10⁻⁷ Z_{AB}. Z_{AB} is the total gas kinetic collision rate per m³ for NO colliding with O₂. In what follows, assume the binary collision model. You do NOT need any results from problem 2 to do this problem!

Print your name here:

a) (20 points) Determine the activation energy, E_A (a constant independent of temperature), for the reaction:



Show all reasoning clearly.

$$R = PZ_{AB}e^{-E_A/RT} \text{ Free formula}$$

$$300 \text{ K: } R = 10^{-7} Z_{AB} \text{ given}$$

$$330 \text{ K } R = 3 \times 10^{-7} Z_{AB} \text{ given}$$

$$10^{-7} Z_{AB} = PZ_{AB}e^{-E_A/(300R)}$$

$$3 \times 10^{-7} Z_{AB} = PZ_{AB}e^{-E_A/(330R)}$$

$$Pe^{-E_A/300R} = 10^{-7} \quad Pe^{-E_A/330R} = 3.0 \times 10^{-7}$$

$$[Pe^{-E_A/330R}] / [Pe^{-E_A/300R}] = 3 \times 10^{-7} / 10^{-7}$$

$$[e^{-E_A/330R}] / [e^{-E_A/300R}] = 3$$

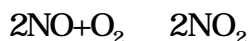
$$E_A/R (1/300 - 1/330) = \ln 3$$

$$E_A = R \ln 3 [(300)(330)/30]$$

$$E_A = 8.314 \text{ joules/mole-deg} (1.099) (3300 \text{ deg})$$

$$E_A = 30142 \text{ joules/mole}$$

b) (10 points) Determine the steric factor, P, for the reaction:



Show reasoning clearly. (P can be assumed independent of temperature)

$$\text{At } 300 \text{ K} \quad PZ_{AB}e^{-E_A/RT} = 10^{-7} Z_{AB}$$

$$Pe^{-E_A/300R} = 10^{-7}$$

$$P = 10^{-7} e^{E_A/300R}$$

$$E_A = 30142 \text{ joules/mole (part a)}$$

$$E_A/300R = 30142/(300)(8.314) = 12.085$$

$$P = 10^{-7} e^{12.085} = 0.0177$$

Print your name here:

Problem 4 (40 points) In the year 2020 you are traveling aboard the starship Columbia when you accidentally go through a “wormhole” and come out in a strange “alternate” universe called Alterland. In this alternate universe the laws of physics and chemistry that you learned in your beloved 2407 chemistry course at Columbia, 22 years earlier, are somewhat altered. For example, the Equipartition Theorem in Alterland can be stated:

Kinetic Energy = kT per degree of freedom per atom or molecule

but the kinetic energy of an atom is still $(1/2)m(C_{\text{rms}})^2$

a) (5 points) Determine the kinetic energy of 1 mole of Helium gas at 300 K in Alterland. Show all reasoning clearly.

$KE = (kT / \text{atom}) \times \# \text{ degrees of freedom}$

For an atom like He, 3 degrees of freedom (x, y, z)

$KE / \text{atom} = 3kT$

$KE / \text{mole} = 3 (N_o k) T$

$KE / \text{mole} = 3RT$

$KE / \text{mole} = (3)(8.314 \text{ joules/mole-deg})(300 \text{ deg})$

$KE / \text{mole} = 7482.6 \text{ joules/mole}$

b) (10 points) If the atomic weight of He is 0.004Kg/mole, determine the root mean square speed of a He atom at 300 K in Alterland. Show all reasoning clearly.

$KE = 3kT$ (see part a)

$(1/2)mc_{\text{rms}}^2 = 3kT$

$c_{\text{rms}} = (6kT/m)^{1/2}$

$c_{\text{rms}} = [6(N_o k)T / (N_o m)]^{1/2}$

$c_{\text{rms}} = (6RT/M)^{1/2}$

$c_{\text{rms}} = [(6)(8.314)(300)/(0.004)]^{1/2} \text{ m/s}$

$c_{\text{rms}} = 1934 \text{ m/s}$

c) (5 points) Derive an expression for the constant volume heat capacity, C_v , for ideal monatomic gases like He, Ne, Xe in Alterland. Show all reasoning clearly.

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At const V, no work done: $dw = -pdV = 0$

$$dE = dQ + dw = dQ$$

$$\left. \frac{dQ}{dT} \right|_V = \left. \frac{dE}{dT} \right|_V$$

$$E = 3RT \text{ per mole}$$

$$\left. \frac{dE}{dT} \right|_V = 3R \text{ per mole}$$

d) (15 points) Derive an expression for the constant pressure heat capacity, C_p , for ideal monatomic gases like He, Ne, Xe in Alterland.

Using the results of part (c) above, determine the ratio of C_p/C_v for monatomic atoms like He etc in Alterland. Show all reasoning clearly.

$$p \text{ constant } dw = -pdV = 0$$

$$dQ = dE - dw$$

$$dQ = dE + pdV$$

$$\left. \frac{dQ}{dT} \right|_p = \left. \frac{dE}{dT} \right|_p + p \left. \frac{dV}{dT} \right|_p$$

$$\text{For 1 mole } V = RT/p$$

$$\left. \frac{dV}{dT} \right|_p = R/p$$

$$E = 3RT \quad \left. \frac{dE}{dT} \right|_p = 3R$$

$$C_p = dQ / dT |_p = 3R + p(R/p)$$

$$C_p = 4R$$

$$\text{From (c) } C_v = 3R$$

$$C_p / C_v = 4R / 3R = 1.33$$

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e) (5 points) Determine the ratio of C_p/C_v for linear diatomics like N_2, O_2 in Alterland. Show reasoning clearly.

For N_2, O_2 5 degrees of freedom

$$KE = 5RT$$

$$C_v = \left. \frac{dE}{dT} \right|_v = 5R$$

$$C_p = \left. \frac{dE}{dT} \right|_p + p \left. \frac{dV}{dT} \right|_p$$

$$C_p = 5R + p (R/p) \text{ (see part d)}$$

$$C_p = 6R$$

$$C_p / C_v = 6R / 5R = 1.20$$

The End