

NAME and ID NUMBER:

There should be **18** pages to this exam, counting this cover sheet. Please check this exam NOW!

There are two formula/data sheets and a periodic chart (with molar masses) at the back of this exam. Books, notes, etc. are not permitted, however calculators are. Not all questions are equally difficult. Spending all your time on one question is generally a bad idea. Problems 1-4 are required. In addition, choose one of either problem 5 or problem 6. Extra credit can be earned if you are able to solve *both 5 and 6*. Note that problem 6 requires use of calculus. Good luck!

GRADING

1. (10 points)

2. (30 points)

3. (15 points)

4. (30 points)

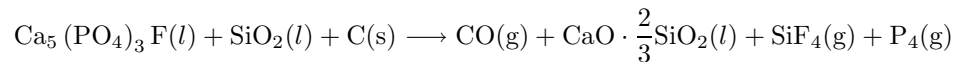
5. (15 points)

6. (15 points)

TOTAL: 115 points

1. (10 points)

Phosphoric acid H_3PO_4 is produced in a three-step process called the *furnace process*, the first step of which is described by the unbalanced reaction



in which three gaseous species, including white phosphorous $\text{P}_4(g)$, are produced.

a. (5 points)

Write the balanced reaction.

b. (5 points)

The reaction in part a) is carried out at high temperature. Suppose the reaction is limited by the amount of coke, $C(s)$, that can be supplied. Once the reaction is completed, the gaseous products are collected in a 50.0 L vessel. The temperature and pressure of the products in the vessel are found to be 2000° and 40 atm, respectively. What minimum mass of silica, SiO_2 , must have been supplied initially?

2. (30 points)

The molecule fluoroethylene is a planar molecule having the formula C_2H_3F (see figure).

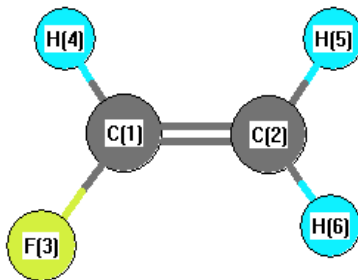


FIG. 1.

a. (10 points)

The internal geometry of the molecule is as follows: $d_{C_1C_2} = 1.33 \text{ \AA}$, $d_{C_1F_3} = 1.35 \text{ \AA}$, $d_{C_1H_4} = 1.10 \text{ \AA}$, $d_{C_2H_5} = 1.08 = d_{C_2H_6} \text{ \AA}$, $\theta_{C_2C_1F_3} = 120.8^\circ$, $\theta_{C_1C_2H_5} = 119.0^\circ$, $\theta_{C_1C_2H_6} = 120.9^\circ$, $\theta_{C_2C_1H_4} = 129.2^\circ$, $\theta_{H_5C_2H_6} = 120.1^\circ$, $\theta_{F_3C_1H_4} = 110.0^\circ$. From this information, determine a set of coordinates for each of the atoms in the molecule. Be sure to indicate *clearly* the coordinate system you have chosen to use. **WARNING!!** The C=C axis does NOT bisect the $F_3C_1H_4$ and $H_5C_2H_6$ angles!

b. (10 points)

The fractional (partial) charges on the atoms are as follows: $\delta_{C_1} = 0.156e$, $\delta_{C_2} = -0.360e$, $\delta_{F_3} = -0.246e$, $\delta_{H_4} = 0.140e$, $\delta_{H_5} = 0.158e$, $\delta_{H_6} = 0.152e$. From this information and your atomic coordinates, calculate the total dipole moment *vector* $\vec{\mu}$ in **Debye**, its magnitude, and indicate the direction of the dipole moment on your chosen coordinate system.

c. (5 points)

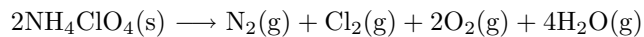
Draw the Lewis structure of the molecule, indicating all nonzero formal charges.

d. (5 points)

Removal of a proton H^+ from the molecule leads to the fluoroethylene anion CH_2F^- . Draw the Lewis structure for this anion, indicating all nonzero formal charges. Be sure to indicate where on the molecule deprotonation occurs. Explain your choice of deprotonation site.

3. (15 points)

Solid ammonium perchlorate NH_4ClO_4 is a thermally labile material used as a rocket fuel to generate the initial thrust needed by the rocket to achieve escape velocity from the Earth's gravitational pull, this velocity being at least 11,200 m/s. In order to achieve this, an initial thrust of approximately 254,000 N (the SI unit of force) is needed. The initial thrust is provided by high pressure gases produced in the detonation reaction



that is initiated by a mechanical shock applied to the solid. Suppose the reaction produces gases at 2000 K that impinge upon a hemispherical rocket shell of radius 1.8 m. What mass (in grams) of ammonium perchlorate is needed to produce the initial thrust required for the rocket to reach escape velocity? How many moles of each product gas will be produced? Assume all gases can be treated as ideal gases.

4. (30 points)

The charge-dipole interaction or explaining the balloon-water stream experiment. As we saw in class, a water stream will always be attracted to a charged rubber balloon. Recall that a water molecule has a net dipole moment $\vec{\mu}$, which can be effectively represented as a positive charge $+q$ and negative charge $-q$ at positions \mathbf{r}_+ and \mathbf{r}_- , respectively (see figure). In the present treatment, we will make a few simplifying assumptions. First, the distance between the two charges in the dipole is assumed to remain fixed at a distance d , with $|\mathbf{r}_+| = |\mathbf{r}_-| = d/2$. Second, the dipole is free to rotate about an axis but *only* in the xy plane, i.e. about the z axis. Consider an additional charge Q at a position \mathbf{R} , as shown in the figure.

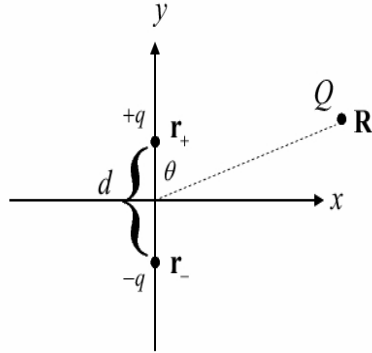


FIG. 2.

a. (5 points)

Write down the total Coulomb energy of this system *relative* to the quantity $-q^2/(4\pi\epsilon_0 d)$ in terms of the charges and the vectors \mathbf{R} , \mathbf{r}_+ and \mathbf{r}_- . **Note:** Your answer will likely involve magnitudes of vector differences.

b. (5 points)

Introduce a vector $\vec{\delta}$ such that $\vec{\delta} = \mathbf{r}_+ - \mathbf{r}_-$ and $\delta \equiv |\vec{\delta}| = d$. Show that

$$\mathbf{r}_+ = \frac{1}{2} \vec{\delta} \quad \mathbf{r}_- = -\frac{1}{2} \vec{\delta}$$

and express your answer for part a) in terms of the charges and the vectors \mathbf{R} and $\vec{\delta}$.

c. (10 points)

Treating the quantity d^2/R^2 as negligible, i.e. $d^2/R^2 \ll 1$, where $R = |\mathbf{R}|$ (noting, however, that d/R *cannot* be neglected), and using the approximation

$$\frac{1}{\sqrt{1 \pm x}} \approx 1 \mp \frac{1}{2}x$$

express your Coulomb energy in part b) in terms of the charges, R , d , and the angle θ .

d. (5 points)

Show that your expression in part c) can be either attractive or repulsive depending on the orientation of the dipole in the coordinate system, i.e. on the value of θ and the sign of Q . Indicate when the energy is attractive and when it is repulsive.

e. (5 points)

On the basis of your analysis in parts c) and d), provide an explanation of why the water stream is always attracted to the charged balloon.

5. (15 points)

Consider an ideal gas in a noncubic (rectangular) box in which the lengths L_x , L_y , and L_z in the x , y , and z directions satisfy $L_x = L_y = 2L_z$. The volume of the box is $V = L_x L_y L_z$. The basic definition of the pressure as force per unit area allows us to define directional pressures P_x , P_y and P_z , where, for example,

$$P_x = \frac{F_{x,\text{wall,tot}}}{A_x}$$

Here $F_{x,\text{wall,tot}}$ is the total force on the walls perpendicular to the x -axis and A_x is the area of one of these walls, i.e. $A_x = L_y L_z$. Similar definitions hold for P_y and P_z :

$$P_y = \frac{F_{y,\text{wall,tot}}}{A_y} \qquad P_z = \frac{F_{z,\text{wall,tot}}}{A_z}$$

In a cubic box, it is clear, due to the isotropy of the system, that $P_x = P_y = P_z$. Using a kinetic theory analysis as was done in class, determine how P_x , P_y and P_z are related for the rectangular box?

6. **(15 points)**

The Maxwell-Boltzmann speed distribution for a two-dimensional homogeneous system is given by

$$f(u) = Aue^{-mu^2/2k_B T}$$

where m is the mass of a particle in the system, u is its speed, k_B is Boltzmann's constant, T is the temperature, and A is a constant that needs to be determined.

a. **(5 points)**

Derive an expression for the most probable speed.

b. (5 points)

Since $u \in [0, \infty)$, i.e. $u \geq 0$ only is allowed, the distribution clearly satisfies the required condition $f(u) \geq 0$ for all u , as a probability distribution should. The unknown constant A is determined by requiring that

$$\int_0^{\infty} f(u) du = 1$$

Use this condition to derive an expression for A .

c. (5 points)

Suppose the system is composed of nitrogen gas N_2 at a temperature of 40°C . Calculate the probability that a molecule chosen at random will have a speed within an interval of 5000 cm/s larger than the most probable speed.

POSSIBLY USEFUL INFORMATION

$$N_0 = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$R = 8.31441 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 0.082057 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$k_B = 1.38066 \times 10^{-23} \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 1.36262 \times 10^{-25} \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$e = 1.60219 \times 10^{-19} \text{ C} \qquad \epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$$

Some conversion factors

$$1 \text{ \AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$$

$$1 \text{ L} = 10^{-3} \text{ m}^3 = 10^3 \text{ cm}^3$$

$$1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$$

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mm Hg at } 0^\circ\text{C}$$

$$1 \text{ Pa} = 1 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$$

$$1 \text{ L} \cdot \text{atm} = 101.325 \text{ J}$$

$$1 \text{ D} = 3.336 \times 10^{-30} \text{ C} \cdot \text{m}$$

Formulas

$$E_{\text{Coul}} = \frac{Q_1 Q_2}{4\pi\epsilon_0 R}$$

$$\vec{\mu} = \sum_{i=1}^N Q_i \mathbf{r}_i \qquad \mu(D) = \frac{\delta \times R(\text{\AA})}{0.2082 \text{ \AA} \cdot \text{D}^{-1}} \quad (\text{for a diatomic of bond length } R)$$

$$\Delta = \Delta E_{\text{AB}} - \sqrt{\Delta E_{\text{AA}} \Delta E_{\text{BB}}} \qquad \chi_{\text{A}} - \chi_{\text{B}} = 0.102\sqrt{\Delta}$$

$$P = \frac{F}{A} \qquad PV = nRT \qquad \left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

$$KE = \frac{1}{2}mv^2 \qquad \langle \Delta r^2 \rangle = 6Dt \qquad RT = \frac{1}{3}M\langle u^2 \rangle$$

$$A = \sum_{i=1}^N A_i p_i \qquad \rho = \frac{m}{V} \qquad V_m = \frac{A}{\rho}$$

$$X_1 = \frac{n_1}{n_1 + n_2} \qquad X_2 = \frac{n_2}{n_1 + n_2}$$

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{N_{\text{A}}}{N_{\text{B}}} \sqrt{\frac{M_{\text{B}}}{M_{\text{A}}}} \qquad Z_{\text{w}} = \frac{N}{4V} \sqrt{\frac{8RT}{\pi M}} A \qquad Z_1 = \frac{4N}{V} d^2 \sqrt{\frac{\pi RT}{M}}$$

Mathematics

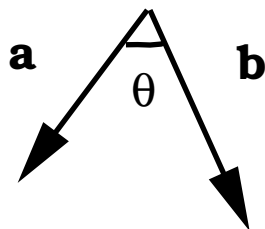


FIG. 3.

$$\mathbf{a} = (a_x, a_y, a_z)$$

$$|\mathbf{a}| = \sqrt{a_x^2 + a_y^2 + a_z^2}$$

$$\mathbf{a} \cdot \mathbf{b} = a_x b_x + a_y b_y + a_z b_z$$

$$\mathbf{a} + \mathbf{b} = (a_x + b_x, a_y + b_y, a_z + b_z)$$

$$|\mathbf{a} + \mathbf{b}| = \sqrt{|\mathbf{a}|^2 + |\mathbf{b}|^2 + 2\mathbf{a} \cdot \mathbf{b}}$$

$$\theta = \cos^{-1} \left[\frac{\mathbf{a} \cdot \mathbf{b}}{|\mathbf{a}| |\mathbf{b}|} \right]$$

$$\cos^2 x + \sin^2 x = 1$$