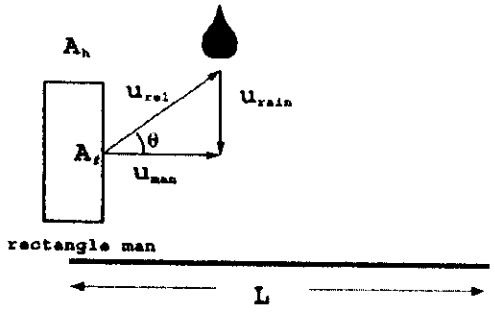
1. Describe the first, second and third laws of thermodynamics. 10%

2. The synthesis of glucose directly from CO_2 and H_2O and the synthesis of proteins directly from amino acids are both non-spontaneous processes under standard conditions. Yet these processes must occur in order for life to exist. In light of the second law of thermodynamics, how can life exist? 10%

3. When molecules collide, do they collide with enough violence to shatter bonds? Sometimes yes, sometimes no. Take H_2 as an example. The bond dissociation energy of H_2 is 436 kJ/mol. (a) At what temperature is the thermal energy (defined as the average kinetic energy) equal to the bond dissociation energy? (b) Is a H_2 molecule likely to dissociate at STP? (Boltzmann's constant $k=1.3807\times10^{-23}$ JK^{-1}) 10%

4. Although the process of dissolution of helium gas in water is favored in terms of energy, helium is only very slightly soluble in water. What keeps this gas from dissolving in great quantities in water? 10%

5. Should you run or walk in the rain in order to keep yourself dry? This question can be treated with the kinetic molecular theory of gases for describing the collisions of gas particles with the wall. Assume that a man described by rectangular shape (the rectangle man) as shown in the figure need to cross a street with length L in the rain. The rectangle man has an upward facing cross sectional area of A_h, and a forward facing cross sectional area of A_f. Raindrops are assumed to fall vertically with a constant speed u_{rain} and the number of raindrops per unit volume is ρ.



The total number of raindrops falling on you can be shown to be

$$\rho L\ (A_f + A_h\ u_{rain}/u_{man}).$$

Interpret the physical meaning of each term in the formula.

According to this formula, should you run or walk in the rain? Does that make a big difference? The typical terminal speeds for raindrops range from 6km/h to 30 km/h (1 m/s to 6 m/s). 10%

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6. In a closest packed structure of spherical atom X, there are octahedral holes and tetrahedral holes. (a) If all tetrahedral holes are all filled with spherical atom T what is the empirical formula of this compound? (b) If all octahedral holes are all filled with M and half of the tetrahedral holes are filled with T, what is the empirical formula of this compound? (c) If the diameter of X is d_X what is the range of the diameter of T that could fit inside the tetrahedral hole? (d) If the diameter of M is d_M what is the range of the diameter of M that could fit inside the octahedral hole? 10%

7. Complex $Ti(H_2O)_6^{+3}$ (Ti is an element in Group IVb, the second element in the first row of transition metal) can absorb visible light in the yellow-green region. (a) Explain why and how this complex absorbs visible light considering the electronic structure. (b) What kind of magnetic property you would expect for this complex? (c) For a complex $Co(en)_2Cl_2^+$, (where en is ethylene diamine) draw all isomers and identify isomers with optical activity. 10%

8. The reaction between methane and chlorine to produce methyl chloride and hydrogen chloride is accelerated by the absorption of light inducing formation of Cl atoms. Cl atoms can catalyze the reaction according to the proposed mechanism: (i) $CH_{4\,(g)} + Cl_{(g)} \rightarrow CH_{3\,(g)} + HCl_{(g)}$ ($\Delta H° = +4$ kJ/mol; $E_a = 17$ kJ/mol), (ii) $CH_{3\,(g)} + Cl_{2\,(g)} \rightarrow CH_3Cl_{(g)} + Cl_{(g)}$ ($\Delta H° = -109$ kJ/mol; $E_a = 4$ kJ/mol). Answer the following questions. (a) Bond enthalpy for Cl_2 is 242 kJ/mol, determine the longest wavelength of light that is energetic enough to cause reaction to occur. In which portion of the spectrum is this light found? (b) Sketch a quantitative energy profile for the catalyzed reaction for steps in the proposed mechanism. (c) Estimate E_a for the reaction $CH_{4\,(g)} + Cl_{2\,(g)} \rightarrow CH_{3\,(g)} + HCl_{(g)} + Cl_{(g)}$. (Planck's constant, $h = 6.626 \times 10^{-34}$ J s) 10%

9. When phosphorus reacts with excess chlorine gas, the compound phosphorus pentachloride (PCl_5) is formed. In the gaseous and liquid states this substance consists of PCl_5 molecules, but in the solid state it consists of a 1:1 mixture of PCl_4^+ and PCl_6^- ions. (a) Predict the geometric structures of PCl_5, PCl_4^+ and PCl_6^-. Hyperconjugation is used to explain the molecule with some atoms becoming exceed the octet rule. (b) How hyperconjugation is applied for PCl_5? (c) Isohypophosphonic acid $H_4P_2O_6$ is triprotic acid and diphosphonic acid $H_4P_2O_5$ is a diprotic acid. Draw Lewis structures for these acids that are consistent with their behavior as acids. 10%

10. An ion having a 4+ charge and a mass of 49.9 amu has two electrons with $n = 1$, eight electrons with $n = 2$, and ten electrons with $n = 3$. Supply the following properties for the ion. (a) the atomic number. (b) total number of each s, p and d electrons (three answers). (c) the number of neutrons in the nucleus. (d) the mass of 3.01×10^{23} atoms (e) the ground-state electron configuration of the neutral atom. 10%

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