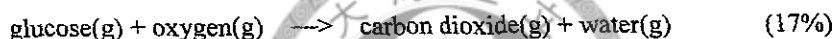


1. (a) A hiker caught in a rainstorm might absorb 1.00 Liter of water in his clothing. If this amount of water is evaporated quickly at 20°C, how much heat would be required for this process?

(b) If all this heat were removed from the hiker (assuming that no significant heat was generated by metabolism during this time), what drop in body temperature would the hiker experience? The clothed hiker weighs 60 kg, and you can approximate the heat capacity of hiker and clothes as equal to that of water.

(c) How many grams of glucose ($C_6H_{12}O_6$ in cyclic form) would the hiker have to metabolize quickly to replace the heat of evaporating 1.00 L. of water so that his temperature would not change? For the present situation, you may approximate the heat of reaction by the following gaseous reaction:



The available informations for this problem are:

Heat of vaporization of liquid water at 20°C: 2450 kJ/kg

Specific heat capacity of liquid water: 4.18 kJ/(K kg)

The average bond dissociation energies (in kJ/mol): C-C: 344; C-O: 350;

C=O: 725; C-H: 415; O-H: 463.

2. For the following consecutively related statements, choose the word or words inside the parentheses that serve to make a correct statement. Each statement has at least one, and may have more than one, correct answer.

(a) According to the second law of thermodynamics, a spontaneous process, such as a balloon filled with hot gas cooling to the surroundings at constant pressure, will always occur (adiabatically, reversibly, irreversibly, without work done).

(b) Associated with such a process, there is always an increase in entropy of (the system, the surroundings, the system plus the surroundings, none of these).

(c) For the example given, the heat gained by the surroundings is just equal to the negative of the (internal energy change, enthalpy change, entropy change, Gibbs free energy change) of the system.

(d) To return a system to its initial state requires from the surroundings an expenditure of entropy whose magnitude is (greater than, equal to, less than) that which is gained during the spontaneous process. (8%)

3. What is the pH of pure water at 37°C? The available informations for this problem are: the ionization constant of water is 1.0×10^{-14} at 25°C, and its $\Delta H^0 = 55.8$ kJ/mol.

One also knows that at constant pressure $\frac{d \ln K_{eq}}{d(1/T)} = -\frac{\Delta H^0}{R}$ in which $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$. (9%)

4. The hard-sphere diameter σ of an H_2 molecule is 2.5 \AA ($2.5 \times 10^{-8} \text{ cm}$). For H_2 gas at 1 atm and 0°C , calculate the following quantities:

- The root-mean-square speed and mean speed of the H_2 molecules.
- The number of H_2 molecules in 1 cm^3 of the gas.
- The number of collisions each H_2 molecule encounters in 1 second.
- The mean free path of an H_2 molecule. (16%)

The informations you may need for this problem are the following constants:

$$k = \text{Boltzmann constant} = R/N_A = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1}$$

$$R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} = 8300 \text{ g m}^2 \text{ s}^{-2} \text{ K}^{-1} \text{ mol}^{-1} = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

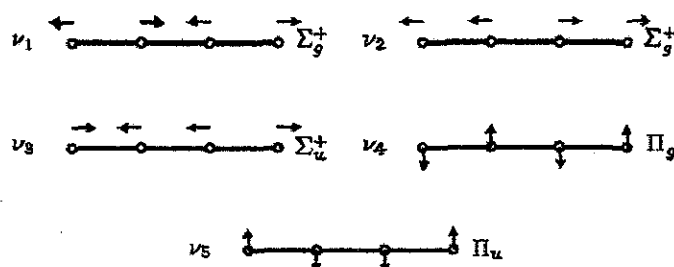
$$N_A = 6.02 \times 10^{23} \text{ molecule mol}^{-1},$$

and also the following equations:

$$\langle v \rangle = \left(\frac{8kT}{\pi m} \right)^{1/2}, \quad \langle v^2 \rangle = \frac{3kT}{m}, \quad z = \sqrt{2} \pi \frac{N}{V} \sigma^2 \langle v \rangle, \quad l = \frac{\langle v \rangle}{z}$$

5. What is the magnitude of the angular momentum for the electrons in 3s, 3p and 3d orbitals? How many radial and angular nodes are there for each of these orbitals. (10%)

6. Cyanogen is a symmetrical linear molecule. The seven normal modes of cyanogen, C_2N_2 , are shown in the following figure:



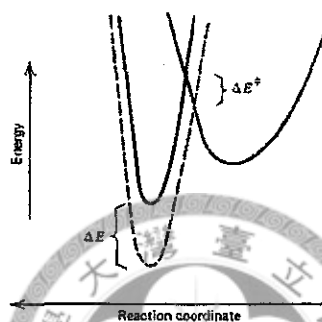
Which are doubly degenerate vibrations? Which vibrations are infrared active? Which vibrations are Raman active? (10%)

7. A simple model to depict the interdependence of $\log k$ (the rate constant) and $\log K$

(the equilibrium constant) is shown in the accompanying figure. One set of curves depicts the energy along the reaction coordinate for $\text{XH}+\text{Y}\rightarrow\text{X}+\text{HY}$ and the other set for $\text{XH}+\text{Y}'\rightarrow\text{X}+\text{HY}'$. Assume that each curve is a harmonic well and that the two product curves are merely shifted vertically. Show that for a small changes

$$\Delta E^\ddagger = B\Delta E$$

where B is a constant. (10%)



8. Identify each statement as either true or false. If a statement is true only under special circumstances, label it as false. (20%)

- Electrons can exhibit both wavelike and particlelike behavior.
- The energy eigenvalues for the H atom in the Schrodinger equation are identical with those in the Bohr theory.
- The angular momentum eigenvalues for the H atom in the schrodinger equation are identical with those in the Bohr theory.
- There is a one-to-one correspondence between the states of the H atom in the Bohr theory and the states of the H atom in quantum mechanics.
- Electrons in a multielectron atom move exactly like electrons in a hydrogenlike atom with the appropriate nuclear charge.
- The total electronic angular momentum of a diatomic molecule is a good quantum number.
- In the self-consistent field calculation such as Hartree-Fock method, if the method were carried out to exact consistency, a correct energy eigenvalue would be obtained.
- Although part of the electronic energy in the Born-Oppenheimer approximation is kinetic energy, this energy acts as a potential energy for nuclear motion.
- A methane molecule has nine vibrational normal modes.
- The rate of a forward reaction can depend on the concentrations of substances other than the substances in the stoichiometric equation.