Attentions:

a) Answers should appear in order in the answer booklet. Each answer should be preceded with its question number/code. Answers not preceded with question numbers/codes will not be credited.

b) Pay attention to the sign and unit of your answers.

c) The following values may be of some use: exp(1.00) = 2.718; exp(2.00) = 7.389; exp(3.00) = 20.09; exp(5.00) = 148.4; ln(2.00) = 0.6931; ln(3.00) = 1.099; ln(5.00) = 1.609; 1 L-atm = 101.325 J; R = 0.08206 L-atm/K-mol = 8.3145 J/K·mol;

1.(8%) A 3.00-g sample of methanol is burned in a constant-volume bomb calorimeter that has a heat capacity of 2.50 kJ/°C and contains 1195 g of water. The burning results in a rise of water temperature from 21.00 °C to 25.00 °C. Calculate the molar heat of combustion of methanol. (The specific heat of water is 4.184 J/g-°C; C=12.01, H=1.008, O=16.00)

2.(13%) (a) Describe the kinetic molecular theory of gases in less than 15 words. (b) Write down at least three assumptions on which the kinetic molecular theory of gases is based? (c) What is gas pressure according to the theory? What are the two factors on which gas pressure depend? (d) What is the molecular interpretation of temperature according to the theory? (e) Can gas pressure be directly related to gas density? Explain. (f) Calculate the root-mean-square speeds (in m/s) of helium atoms at 25.0°C. (He=4.003)

3.(7%) (a) The reaction between X and Y is first order in X and second order in Y. Write down the rate expression of the reaction and determine the units of its rate constant. (assume time in minutes) (b) Two reactions contribute to the hydrolysis of amino-acid esters (AE) in base: (1) hydroxy ion reacting with the protonated ester (HAE^+) and (2) hydroxy ion reacting with the unprotonated ester (AE). The rate constants at 25.00 °C for the protonated and unprotonated esters are 1500 M^{-1}-min^{-1} and 40.0 M^{-1}-min^{-1}, respectively. Assume that when the pH of 0.0200 M AE solution is adjusted to pH 10.00, the concentrations of HAE^+ and AE measured at a certain time in the experiment are 5.0×10^{-4} M and 1.95×10^{-2} M, respectively. (i) Find the rates of the protonated the unprotonated reactions, respectively. (ii) Based on the rates obtained in (i), explain the large difference in concentration for HAE^+ and AE in the solution.

4.(6%) (a) A gas expands from 3.00 L to 6.00 L at constant temperature. Calculate the work (in joule) done by the gas if it expands (i) against a vacuum and (ii) against a constant pressure of 1.00 atm. (b) If, instead, during the expansion against a constant pressure of 1.00 atm, there is a heat transfer of 100 J from the gas to the surroundings. Calculate the change in energy (in joule) of the system.

5.(29%) For this question, no credit will be given for translation only. (a) Without use of equations, define the following terms in less than 25 words each: (i) energy, (ii) thermal energy, (iii) heat, (iv) enthalpy, (v) thermochemistry, (vi) thermodynamics, (vii) work, (viii) internal energy, (ix) specific heat of a substance, (x) heat capacity of a substance. (b) Define the following quantum chemistry terms in less than 25 words each. Equations may be used. (i) operator, (ii) basis, (iii) eigenvector, (iv) eigenvalue, (v) wave function, (vi) orthogonality, (vii) Schrödinger equation, (c) how are *eigenvalues* and *spectrum* related?

6.(18%) (a) Two different reactions are performed, one involving reactant A only and the other reactant B only. The table below shows the changes in reaction rate with the concentrations of reactants A and B, respectively. For example, for the first experimental result of A, the table shows that at [A] of 1.0×10^{-2} M, the reaction rate was 0.20×10^{-5} M/sec. Determine the order and rate constant for each of the two different reactions.

Reactant	Concentration ($\times10^2$, M)	Rate ($\times10^5$, M/sec)	Reactant	Concentration ($\times10^3$, M)	Rate ($\times10^8$, M/sec)
A	1.00	0.200	B	1.00	3.00
A	2.00	0.400	B	2.00	12.00
A	4.00	0.800	B	4.00	48.00
A	12.00	2.400	B	8.00	192.00

(b) If the initial concentration of A was 0.200 M, what is its concentration after 8.333 min? (c) How long (in sec) will it take for the concentration of A to decrease from 0.200 M to 0.0500 M? (d) If A is radioactive, calculate its half-life (in sec)? (e) If the initial concentration of B is 1.00 M, calculate its concentration after 100 sec. (f) Use any two different initial concentrations of B to show whether the half-life of its reaction depends on the initial concentration of B or not. (Known rate equations include: (1) $[A]_0 - [A] = kt$; (2) $1/[A] = 1/[A]_0 + kt$; (3) $1/[A]^2 = 1/[A]_0{}^2 + 2kt$; (4) $\ln([A]_0/[A]) = kt$.)

7.(6%) An oxygen container of 6.00 L has an initial pressure of 20.0 bar. Show your derivation of equation and calculate the amount of heat needed to supply to the gas by a thermostat when half of the gas is allowed to escape slowly at a constant temperature of 20.0°C.

8.(13%) (a) For 2.00 moles of helium gas occupy 6.00 L at 26.85°C. Calculate the pressure (in atm) of the gas using (i) the ideal gas equation and (ii) the van der Waals equation (For He, a=0.034, b=0.0237). (b) The van der Waals equation of state can be expressed as $(P + (a/V_M^2))(V_M - b) = RT$. At the critical point, one has $(\partial p/\partial V_M)_T = 0$ and $(\partial^2 p/\partial V_M^2)_T = 0$. By using the critical values of pressure, P_c, kilomolar volume V_{Mc}, and temperature T_c, rewrite the equation in terms of reduced variables.

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