Attentions:

a) **Do not** leave your answers in the table on the first page of the answer booklet. Write all your answers in the second and subsequent pages of the answer booklet.
b) 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.
c) No explanation or calculation is required in the answer to the multi-select question.
d) Pay attention to the sign and unit of your answers.
e) 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;

I. Multi-select question (44%)

Choose one or more answers from the list of answers provided for each question below. Penalty of 50% credit to the correct answer will be applied for the incorrect choice. No penalty will be applied for failure to choose the correct answer, though.

1. For the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$,
   (A) The amount of $NO_2$ in the reaction container is four times the amount of $O_2$ regardless how the reaction mixture is prepared for the reaction to occur.
   (B) At the moment when $N_2O_5(g)$ is first transferred to the empty reaction container, the rate of disappearance of $N_2O_5$ is more than two times the rate of formation of $O_2$.
   (C) At any instant, the rate of formation of $NO_2$ is two times the rate of disappearance of $N_2O_5$.
   (D) The reaction is a second-order reaction, just like any reactions of $2M_2N_5 \rightarrow 4MN_2 + N_2$.
   (E) If the measured initial rates are $2.4\times10^{-6}$ M/sec and $4.8\times10^{-6}$ M/sec for the initial concentrations of $N_2O_5$ of 0.0050 M and 0.010 M, respectively, the overall reaction order is one.
   (F) The activation energy of the reaction may be derived from measuring the rate constants at two different temperatures.

2. Which of the following statements related to chemical bonding is (are) correct?
   (A) The hybrid orbital used by the N atom in urea, $H_2NCONH_2$, is $sp^3$.
   (B) $H_2S$ has greater ionic character than $H_2O$.
   (C) The bond enthalpies (kJ/mol) of C-H, C-C, C=C, C-Br, H-Br, and Br-Br are 412, 348, 612, 276, and 366, and 193, respectively. The heat released when ethane, $CH_2=CH_2$, reacts with HBr to produce $CH_3CH_2Br$ is 58 kJ/mol.
   (D) Highly electronegative atoms have low ionization energies and high electron affinities.
   (E) $NO_2$ is not a radical.
   (F) The electronic configuration in the oxide ion in BaO is $[He]2s^22p^6$.

3. Which of the following statements is (are) correct?
   (A) Electron diffraction by a crystal can support de Broglie's hypothesis of the wave nature of matter.
   (B) Ultraviolet light, microwaves, and gamma rays travel through empty space at different speed.
   (C) Speeding tickets based on the radar reading are uncertain because of the Heisenberg uncertainty principle.
   (D) People have difficulty in measuring both the position and velocity of objects in everyday life.
   (E) The kinetic energy of the electrons ejected by the incident radiation increases with the radiation intensity.
   (F) For the hydrogen atom, the Lyman series of lines are found only in the ultraviolet region of the spectrum.

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4. Which of the following kinetics statements is (are) correct?
(A) If the rate of a reaction increases by a factor of 8 when the concentration of a reactant increases by a factor of 2, the order of the reaction with respect to this reactant is 4.
(B) Decomposition of nitrous oxide is a zero-order reaction.
(C) The rate law of a reaction can be predicted from reaction stoichiometry.
(D) The rate law of a zeroth-order reaction is rate = $k$.
(E) An enzyme-catalyzed reaction may appear to be zero-order if the number of enzyme molecules in the reaction is limited in relation to substrate molecules.
(F) Even complex biological processes may exhibit Arrhenius behavior within certain temperature ranges.

5. Which of the following processes result(s) in an increase in entropy?
(A) Expanding 1 mol of oxygen gas isothermally to twice its original volume.
(B) Doubling the pressure of 1 mol of nitrogen gas isothermally.
(C) Compressing 1 mol of nitrogen gas isothermally to half of its original volume.
(D) Increasing the temperature of 1 mol of argon gas at constant pressure.
(E) Freezing the crystal of 1 g of NaCl.
(F) Water of 1 mL losing energy reversibly at 25°C.

6. Which of the following statements is (are) correct?
(A) Boron is not a metalloid.
(B) In quantum systems, as the mass of the particle in a one-dimensional box becomes larger, the separation between neighboring energy levels decreases.
(C) The total number of orbitals in a shell with principal quantum number 4 is 8.
(D) The total number of nodal planes present in the orbitals having the set of quantum numbers $n$=3 and $\ell$=2 is 10.
(E) The probability of finding an electron at the nucleus in a p-orbital is zero.
(F) The zero-point energy in 1,3,5,7-octatetraene is larger than in 1,3-butadiene.

7. The reaction of NO with $Cl_2$ proceeds in a fixed container as follows.

Step 1: $NO(g) + Cl_2(g) \rightarrow NOCl_2(g)$ Fast
Step 2: $NOCl_2(g) + NO(g) \rightarrow 2NOCl(g)$ Slow
Overall: $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$

Which of the following statements is (are) correct?
(A) The forward rate equals the reverse rate when the reaction is in equilibrium.
(B) The reaction rate is determined by the collision between NO(g) and $Cl_2(g)$ molecules.
(C) Increasing the concentration of $Cl_2(g)$ will increase the reaction rate.
(D) Removing NOCl(g) from the reaction mixture will increase the reaction rate.
(E) The reaction is a second-order reaction.
(F) The unit of $k$ in the rate law of the reaction is L/mol-s. if the concentration of the reactant is expressed in mol/L and the rate in mol/L-s.

接次頁

8. Which of the following thermodynamics statements is (are) correct?
(A) A closed system cannot exchange energy with the surroundings.
(B) The work done by a construction worker, weighing 60 kg, who climbs to the roof a 50-m tall building is about 29 kJ.
(C) A system at lower temperature has a greater internal energy than the same system at a higher temperature.
(D) The internal energy of molecules is stored only as molecular potential energy.
(E) The total motional contribution to the molar internal energy of gaseous $H_2O$ at 25°C is 7.43 kJ/mol.
(F) The equipartition theorem states that every degree of freedom that appears only quadratically in the total energy contributes R to the system's heat capacity.

9. A particle trapped inside a one-dimensional box
(A) is likely to be found at one position than another in classical systems.
(B) cannot moves at any speed within the box in classical systems.
(C) only occupy certain energy levels if the box size is on the scale of a few nanometers.
(D) can have zero energy if the box size is on the scale of a few nanometers.
(E) may never be detected at certain positions if the box size is on the scale of a few nanometers.
(F) results in four wavelengths equaling the size of the box for $n$=4, if the box size is on the scale of a few nanometers.

II. Physical chemistry concepts and calculations

10. Discuss in detail (a) (i) collision theory and (ii) transition state theory taught in chemical kinetics; (b) (i) Hess's law and (ii) Born-Haber cycle taught in thermodynamics. (20%)

11. Assume 2.000 mol $O_2$(g) at 298.0 K and 1.00 atm behaves ideally. Calculate (i) the change in internal energy and (ii) the final temperature of the oxygen gas when 200.0 J of energy is transferred as heat to the gas at (a) constant volume; (b) constant pressure. (11%)

12. (a) A sample of ideal gas at 244 K and 2.00 atm expands from 10.0 L to 20.0 L by two different paths. Path A has two parts. In the first step, the gas is cooled at constant volume to 1.00 atm. In the second step, the gas is heated and allowed to expand against a constant external pressure of 1.00 atm until its volume is 20.0 L and T = 244 K. Path B is an isothermal, reversible expansion to reach a final pressure of 1.00 atm. Calculate for each path (i) the work done, (ii) the heat transferred, and (iii) the change in internal energy. (b) Discuss the difference in the calculated results obtained in (a) between Paths A and B and explain how the concept of state function is revealed. (c) Can the results obtain in (a) be used to support the first law of thermodynamics? Explain. (13%)

13. A nonspontaneous reaction can be driven to occur in biological systems by using a reaction that produces a lot of entropy in the surrounding for building and maintaining their intricate functions. Use any biological reactions as examples to discuss the physical chemistry principle behind the drive and address the related Gibbs free energy changes in biological systems. (For example, the hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) is the reaction used most frequently by organisms to couple and drive nonspontaneous reactions. Eating food that contains glucose can help to restore ADP back to ATP by combustion of glucose in our bodies. However, you can use whichever the reaction you know the best to answer this question.) (12%)

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