注意事項：
1. 請勿在答案本第一頁(制式表格)中作答。所有答案皆須寫在答案本第二頁之後。
2. Part I 和 Part II(亦即所有選擇題)必須依題號次序標示題號後作答，未標示題號或未依題序答題者，不予記分。

I. 單選題(每題 1.5 分)
No penalty will be applied for incorrect answers.

1. For a reaction with the rate law: Rate = $[X]^2 [Y]^1 [Z]^0$, the overall order of the reaction is
(A) 0　(B) 1　(C) 2　(D) 3　(E) 4　(F) none of the above

2. Which one of the following sets of quantum numbers is not possible?
(A) $n=4$ $l=1$ $m_l=1$ $m_s=-1/2$　(B) $n=4$ $l=3$ $m_l=-2$ $m_s=+1/2$
(C) $n=3$ $l=2$ $m_l=-3$ $m_s=+1/2$　(D) $n=3$ $l=0$ $m_l=0$ $m_s=-1/2$
(E) $n=2$ $l=0$ $m_l=0$ $m_s=+1/2$　(F) none of the above

3. The process $H_2O(g) \leftrightharpoons H_2O(l)$ is exothermic at a pressure of 1.0 atm and a temperature of 370 K. Which of the following statements about the signs of q and w is correct?
(A) q and w are negative　(B) q is positive, w is negative　(C) q and w are both zero
(D) q is negative, w is positive　(E) q and w are both positive

4. The number of electrons in the 3rd principal energy level ($n = 3$) of a phosphorus atom is
(A) 2　(B) 3　(C) 4　(D) 5　(E) 6　(F) 8

5. CO_2 is expanded against a pressure of 1.0 atm at constant temperature from 1.0 to 3.5 liters. The work for the expansion is
(A) 0 L·atm　(B) 2.5 L·atm　(C) –2.5 L·atm　(D) 3.5 L·atm
(E) –3.5 L·atm　(F) none of the above

6. The rate constant k depends on
(A) the order of the reaction.　(B) the concentration of the reactant.　(C) the temperature.
(D) the concentration of the product.　(E) none of the above

7. Which one of the following statements about standard states is incorrect?
(A) The standard state of an element is the form in which it is stable at 1 atm and a specified temperature, usually 25°C.
(B) The standard state of a gaseous compound is the gas at a pressure of 1 atmosphere.
(C) The standard state of a liquid compound is the pure liquid.
(D) The standard state of a solid compound is the pure solid.
(E) The standard state of an aqueous solute is a saturated solution in water.
(F) none of the above

8. The maximum number of electrons that occupy an energy level described by the principal quantum number, n, is
(A) $n-1$　(B) n　(C) $n+1$　(D) $2n$　(E) $2n^2$　(F) n^2

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9. Instant cold packs are a convenient direct replacement for crushed ice used as first aid on sport injuries when ice is unavailable Their temperatures are lowered when water in a pocket inside a bag of ammonium nitrate solids is broken by squeezing to allow the solids to be dissolved. Which of the following is true of this dissolution?

(A) $\Delta H < 0$, process is endothermic
(B) $\Delta H > 0$, process is exothermic
(C) $\Delta H > 0$, process is endothermic
(D) $\Delta H < 0$, process is exothermic
(E) $\Delta H = 0$, since the process is adiabatic in the sealed bag
(F) none of the above

For the reaction $X_2 + 2Y_2 \rightarrow 2Z$, the following mechanism has been proposed:

step 1 (very slow) $X_2 + Y_2 \rightarrow Q + Z$
step 2 (slow) $Q + Y_2 \rightarrow Z$

Based on the information, answer the questions 10-12:

10. The molecularity of step 2 is

(A) unimolecular (B) bimolecular (C) termolecular (D) quadmolecular
(E) The information is insufficient to decide the molecularity. (F) none of the above

11. The rate-determining step(s) is(are)

(A) step 1 (B) step 2 (C) both steps (D) the step between step 1 and step 2
(E) the stepp before step 1 (F) The information is insufficient to decide the rate-determining step.

12. The overall rate law is

(A) Rate = $k[X_2]$ (B) Rate = $k[X_2]^2$
(C) Rate = $k[Y_2]^2$ (D) Rate = $k[X_2][Y_2]$
(E) Rate = $k[Q][Y_2]$ (F) Rate = $k[Q]^2$

13. The ground-state electron configuration for an atom of calcium is

(A) $[Kr]5s^2$ (B) $[Ar]4s^2$ (C) $[Ar]3d^2$ (D) $[Ar]4s^13d^1$ (E) $[Kr]4d^2$ (F) $[Kr]5s^14d^1$

14. The mechanism for the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$ is as follows:

$H_2O_2 + I^- \rightarrow H_2O + IO^-$
$H_2O + IO^- \rightarrow H_2O + O_2 + I^-$

The catalyst(s) in the reaction is(are)

(A) H_2O_2 (B) I^- (C) H_2O (D) IO^- (E) I^- and IO^- (F) O_2

The second line in the Balmer series is observed at 486.1 nm. Answer the questions 15-17:

15. The 486.1-nm line is characterized by the electron transitioning from n_x to n_y. Which of the following (n_x,n_y) pairs is correct.

(A) (1,3) (B) (2,3) (C) (2,4) (D) (3,1) (E) (4,1) (F) (4,2)

16. The Balmer series describes the spectral line emissions of the _____ atom.

(A) hydrogen (B) helium (C) sodium (D) carbon
(E) nitrogen (F) oxygen

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II. 單選題(每題 2 分)
No penalty will be applied for incorrect answers.

17. The energy difference between the initial and final levels in the emission process of the 486.1-nm line is
(A) 2.44×10^{18} J　(B) 2.44×10^{21} J　(C) 4.09×10^{-28} J
(D) 4.09×10^{-22} J　(E) 1.07×10^{-48} J　(F) none of the above

18. ΔH is more positive than ΔE by 2.5 kJ/mol for the process $H_2O(l) \leftrightharpoons H_2O(g)$ at 298 K and 1.0 atm. This quantity of energy can be considered to be
(A) the value of ΔH itself　(B) the work done in pushing back the atmosphere
(C) the difference in the H–O bond energy in $H_2O(l)$ compared to $H_2O(g)$
(D) the heat flow required to maintain a constant temperature
(E) none of the above

19. Water has a specific heat of 4.18 J/g·°C. The amount of heat required to raise the temperature of 15.0 g of water from 20.0°C to 100.0°C.
(A) 6270 J　(B) 23.39 kJ　(C) 1254 J　(D) 279 J
(E) 18.37 kJ　(F) 5016 J

20. Based on the following information:
$CH_3OH(l) + (3/2)O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$　$\Delta H° = -726.4$ kJ/mol
$H_2(g) + (1/2)O_2 \rightarrow H_2O(l)$　$\Delta H° = -285.8$ kJ/mol
$C(graph) + O_2 \rightarrow CO_2(g)$　$\Delta H° = -393.5$ kJ/mol
the standard enthalpy of formation of liquid methanol, $CH_3OH(l)$, is
(A) –238.7 kJ/mol　(B) 238.7 kJ/mol　(C) –1,691.5 kJ/mol
(D) 1,691.5 kJ/mol　(E) –47.1 kJ/mol　(F) 47.1 kJ/mol

21. $\Delta H°_{combustion}$ for $H_2(g)$, $C_4H_4(g)$, and $C_4H_8(g)$ are –286 kJ/mol, –2341 kJ/mol, and –2755 kJ/mol, respectively. The $\Delta H°$ for the reaction $C_4H_4(g) + 2H_2(g) \leftrightharpoons C_4H_8(g)$ is
(A) 158 kJ　(B) –158 kJ　(C) 128 kJ　(D) –128 kJ
(E) 414 kJ　(F) -414 kJ

22. The electron in a metal has threshold frequency of 1.25×10^{14} /s for photoelectrons. The binding energy of the electron is
(A) 3.61×10^{17} kJ/mol　(B) 8.32×10^{-20} J/mol　(C) 6.04×10^{-7} J/mol
(D) 1.37×10^{-43} J/mol　(E) 49.9 kJ/mol　(F) 4.16×10^{-20} J/mol

23. The oxygen-oxygen bond strength in hydrogen peroxide is 210 kJ/mol, which is stronger than the oxygen-oxygen single bond energy of 146 kJ/mol. The approximate longest wavelengths of light that can cause these two bonds to be broken are, respectively,
(A) 5.7×10^{-4} m, 8.2×10^{-4} m　(B) 8.2×10^{-4} m, 5.7×10^{-4} m　(C) 4.1×10^{-7} m, 2.9×10^{-7} m
(D) 9.5×10^{-28} m, 1.4×10^{-27} m　(E) 5.7×10^{-7} m, 8.2×10^{-7} m　(F) none of the above

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24. The mass of a proton is about 1800 times the mass of an electron. If both of them have the same kinetic energy,

(A) the wavelength of the proton will be about $\sqrt{1800}$ times longer than the wavelength of the electron.
(B) the wavelength of the electron will be about $\sqrt{1800}$ times longer than the wavelength of the proton.
(C) the wavelength of the proton will be about 1800 times longer than the wavelength of the electron.
(D) the wavelength of the electron will be about 1800 times longer than the wavelength of the proton.
(E) the wavelength of the photon will be roughly equal to the wavelength of the electron.
(F) none of the above

25. The atomic mass of Ne-20 is 19.992 amu. The wavelength associated with a $^{20}Ne^{+}$ ion moving at a velocity of 2.0×10^{5} m/s is

(A) 2.0×10^{-15} cm (B) 1.0×10^{-16} cm (C) 1.0×10^{-13} m
(D) 9.7×10^{12} m (E) 2.0×10^{-18} m (F) 2.0×10^{-11} cm

26. Free halogen atoms may be generated in solution to initiate chemical reactions with light. The change of enthalpy for the generation of free chlorine atoms, $Cl_2(g) \rightarrow 2Cl(g)$, in solution is 242.8 kJ/mol. The longest wavelength of light that will generate free chlorine atoms in solution is

(A) 328.4 nm (B) 656.8 nm (C) 985.2 nm
(D) 492.6 nm (E) 246.3 nm (F) 456.8 nm

27. The hydrogen bonding in the secondary structure of proteins can be denatured by heat. The denaturation process can be best described with

(A) $\Delta H < 0$ and $\Delta S = 0$. (B) $\Delta H = 0$ and $\Delta S > 0$. (C) $\Delta H < 0$ and $\Delta S > 0$.
(D) $\Delta H > 0$ and $\Delta S > 0$. (E) $\Delta H > 0$ and $\Delta S < 0$. (F) none of the above

28. For which order reaction is the half-life of the reaction independent of the initial concentration of the reactant(s)?

(A) zero order (B) first order (C) second order (D) third order
(E) all of these (F) none of these

29. The reaction A → B + C is known to be zero order in A. Its integrated rate law is

(A) $[A] = kt$ (B) $[A] - [A]_0 = kt$ (C) $\frac{[A]}{[A]_0} = kt$ (D) $\ln\frac{[A]}{[A]_0} = kt$
(E) $[A]_0 - [A] = kt$ (F) none of the above

For the reactant X involved in the reaction x X → products, select the reaction order(s) in questions 30-36 that best fit(s) the stated observations.

30. A plot of [X] vs. t is a straight line.

(A) zero order in X (B) first order in X (C) second order in X
(D) all of these (E) none of these

31. A plot of $[X]^2$ vs. t gives a straight line.

(A) zero order in X (B) first order in X (C) second order in X
(D) all of these (E) none of these

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32. [X] is constant.
(A) zero order in X (B) first order in X (C) second order in X
(D) all of these (E) none of these

33. The half-life is constant.
(A) zero order in X (B) first order in X (C) second order in X
(D) all of these (E) none of these

34. The half-life decreases over time.
(A) zero order in X (B) first order in X (C) second order in X
(D) all of these (E) none of these

35. The reaction rate is constant over time.
(A) zero order in X (B) first order in X (C) second order in X
(D) all of these (E) none of these

36. A plot of k vs. $1/T$ gives a straight line (k is the rate constant and T is the reaction temperature in Kelvin).
(A) zero order in X (B) first order in X (C) second order in X
(D) all of these (E) none of these

37. Chlorine reacts with NO to form NOCl. The reaction, NO + $^1/_2Cl_2 \rightarrow$ NOCl, proceeds as follows:

Expt. #	[NO]	[Cl_2]	Initial Rate
1	0.110	0.0320	0.120 M/min
2	0.330	0.0320	1.08 M/min
3	0.220	0.0160	0.240 M/min

Based on the data above, the rate equation for the reaction is
(A) rate = k[NO] (B) rate = $k[NO]^2$ (C) rate = $k[NO][Cl_2]$
(D) rate = $k[NO][Cl_2]^{1/2}$ (E) rate = $k[NO]^2[Cl_2]$ (F) rate = $k[NO]^2[Cl_2]^2$

For the reactant X involved in the reaction x X $\rightarrow$ products, the initial concentration of X, $[X]_0$, is 2.00 M, and the first three successive half-lives are 40.0, 80.0, and 160.0 min. Answer questions 38-39:

38. The rate constant k (without units) is
(A) 5.00×10^{-2} (B) 2.50×10^{-2} (C) 1.25×10^{-2}
(D) 6.25×10^{-3} (E) 1.73×10^{-2} (F) none of the above

39. The instantaneous concentration of X, [X], at t = 55.0 min is
(A) 0.772 M (B) 0.625 M (C) 0.308 M (D) 1.19 M
(E) 0.533 M (F) 0.842 M

40.(12%) Define the following terms used in physical chemistry: (a) polarizability, (b) magnetic susceptibility, (c) electrophoresis, (d) zeta-potential, (e) Fick's first law, (f) Stokes-Einstein relation, (g) dispersion force, (h) Madelung constant.

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41.(5%) For the following types of electromagnetic radiation:
ultraviolet, infrared, radio waves, microwave, visible, and gamma rays
rank them in the order of decreasing energy.

42.(13%) If f is a function of x and y, the change in f, df, is d$f = (\partial f/\partial x)_y dx + (\partial f/\partial y)_x dy$. In addition, for d$f$ = a(x,y)dx + b(x,y)dy, df is exact if $(\partial a/\partial y)_x = (\partial b/\partial x)_y$. Prove the following thermodynamically:
(a) If the volume and composition are constant, discuss and prove that the ratio of the change in energy to the corresponding change in entropy is equal to the temperature of the system.
(b) Discuss and prove that $(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$
(c) Discuss and prove that $(\partial U/\partial V)_T$ is zero for a perfect gas.
(d) Calculate the value of $(\partial U/\partial V)_T$ for a van der Waals gas.

試題隨卷繳回