

類組：化學類 科目：物理化學(1004)

共 10 頁 第 1 頁

※選擇題請在答案卡內作答，非選擇題請在答案卷內作答

一. 選擇題

(一). 單選題，每題 2 分，答錯不倒扣。

1. The ionization energy for hydrogen atom is 13.6 eV. The ionization energy for the ground state of  $\text{Li}^{++}$  is approximately
  - (A) 13.6 eV
  - (B) 27.2 eV
  - (C) 40.8 eV
  - (D) 54.4 eV
  - (E) 122.4 eV
2. Planck's constant has the same units as
  - (A) angular momentum
  - (B) the Hamiltonian
  - (C) frequency
  - (D) quantum number
  - (E) de Broglie wavelength
3. Which of the following is NOT a correct consequence of the Heisenberg Uncertainty principle:
  - (A) The shorter the lifetime of an excited state of an atom, the less accurately can its energy be measured.
  - (B) An electron in an atom cannot be described by a well-defined orbit.
  - (C) The momentum of an electron cannot be measured exactly.
  - (D) Measurement of one variable in an atomic system can affect subsequent measurements of other variables.
  - (E) A harmonic oscillator possesses a zero-point energy.
4. The orbital degeneracy (excluding spin) of hydrogen atom energy levels equals
  - (A)  $n - 1$
  - (B)  $n$
  - (C)  $n + 1$
  - (D)  $2n + 1$
  - (E)  $n^2$

參考用

注意：背面有試題

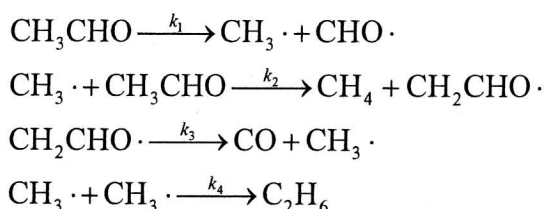
※選擇題請在答案卡內作答，非選擇題請在答案卷內作答

5. Which of the following statements about the hydrogen atom ground state is INCORRECT:
- (A) It is described by the quantum numbers  $n = 1; l = 0; m = 0$ .
  - (B) The electron's angular momentum equals  $h$ .
  - (C) The wave function is spherically symmetrical.
  - (D) The wave function decreases exponentially as a function of  $r$ .
  - (E) The radial distribution function has its maximum at the Bohr radius.
6. In terms of collision theory, the reaction rate constant does NOT depend on which of the following requirements or factors?
- (A) Steric requirement.
  - (B) Minimum energy requirement.
  - (C) Encounter rate.
  - (D) Reaction Gibbs free energy.
  - (E) none of the above.
7. For diatomic molecular partition functions  $q^T$ (translation),  $q^R$ (rotation),  $q^V$ (vibration), and  $q^e$ (electronic). Which one is generally less dependent on temperature?
- (A)  $q^T$
  - (B)  $q^R$
  - (C)  $q^V$
  - (D)  $q^e$
  - (E) all of the above.
8. Consider the reaction  $A \xrightarrow{k} P$ . If the reaction is one-half order with respect to  $[A]$  and  $[A]_0$  is the initial concentration, the half-life of this reaction depends on
- (A)  $[A]_0^{1/2}$
  - (B)  $[A]_0^{-1/2}$
  - (C)  $[A]_0$
  - (D)  $[A]_0^{3/2}$
  - (E) none of the above.

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9. Consider the thermal decomposition of 1 atm of  $(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$  to acetone  $(\text{CH}_3)_2\text{CO}$  and ethane  $(\text{C}_2\text{H}_6)$ , which occurs with a rate constant of  $0.0019 \text{ s}^{-1}$ . After initiation of the reaction, at what time would you expect the pressure to be 1.8 atm?  $\ln(0.6) = -0.51$  and  $\ln(0.4) = -0.916$ .
- (A) 9 s (B) 35 s  
(C) 269 s (D) 3600 s  
(E) none of the above.

10. The Rice-Herzfeld mechanism for the thermal decomposition of acetaldehyde  $(\text{CH}_3\text{CHO})$  is



Using the steady-state approximation, determine the order of rate of methane ( $\text{CH}_4$ ) formation with respect to  $\text{CH}_3\text{CHO}$ ?

- (A)  $-1/2$   
(B) 0  
(C)  $1/2$   
(D)  $3/2$   
(E) none of the above.
11. Obtain an expression for  $\kappa_T$  (isothermal compressibility) for a van der Waals gas.

$V_m$  is the molar volume.

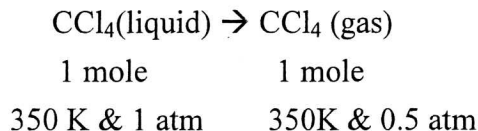
- (A) 0  
(B)  $\frac{-1}{V_m \left[ \frac{2a}{V_m^3} - \frac{RT}{(V_m - b)^2} \right]}$   
(C)  $\frac{1}{\left[ \frac{2a}{V_m^3} - \frac{RT}{(V_m - b)^2} \right]}$   
(D)  $\frac{-1}{V_m \left[ \frac{2a}{V_m^2} - \frac{RT}{(V_m - b)^3} \right]}$   
(E) none of the above.

類組：化學類 科目：物理化學(1004)

共 10 頁 第 4 頁

※選擇題請在答案卡內作答，非選擇題請在答案卷內作答

12. The normal boiling point of liquid  $\text{CCl}_4$  is 350 K at 1 atm and its heat of vaporization is 30.0 kJ/mol. One mole of  $\text{CCl}_4$  is subjected to the following process:



Assume  $\text{CCl}_4(\text{g})$  is considered as ideal. Determine the change in entropy  $\Delta S$  for the system only for the process shown above.  $R = 0.08206 \text{ L-atm K}^{-1} \text{ mol}^{-1} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $\ln(2) = 0.693$ .

- (A) 91.46 J/mol-K  
 (B) 79.93 J/mol-K  
 (C) 13.00 J/mol-K  
 (D) 213.19 J/mol-K  
 (E) none of the above.
13. For the  $\text{N}_2(\text{g}) \rightleftharpoons 2\text{N}(\text{g})$  reaction, the  $\Delta G^\circ = 911 \text{ kJ}$  and  $K_p = 2 \times 10^{-160}$ . The  $K_p$  of  $\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}(\text{g})$  reaction shall be:  
 (A) zero  
 (B) smaller than  $2 \times 10^{-160}$   
 (C) larger than  $2 \times 10^{-160}$   
 (D) equal to  $2 \times 10^{-160}$   
 (E) can not be determined.
14. Which of the following statements about the molecular modelling and computational methods is FALSE?  
 (A) Energy minimisation is used to find a stable conformation for a molecule.  
 (B) Energy minimisation always finds the most stable conformation for a molecule.  
 (C) Molecular mechanics uses equations obeying the laws of classical physics.  
 (D) Molecular mechanics can not predict the molecular orbital energies for a molecule.  
 (E) none of the above.
15. The chemical potential of a system as the pressure increases.  
 (A) Increase (B) Decrease  
 (C) Constant (D) Zero  
 (E) none of the above.

注意:背面有試題

※選擇題請在答案卡內作答，非選擇題請在答案卷內作答

(二). 多選題，ABCDE 每一選項單獨計分，每題 5 分，答錯不倒扣。

16. In terms of statistical thermodynamics, which of the following statements is TRUE?

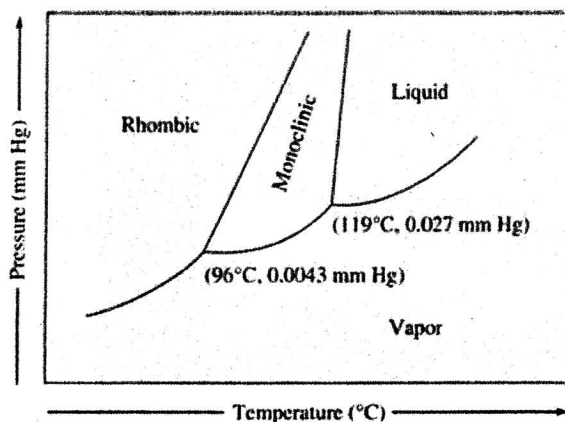
- (A) At 1 bar and 300 K, 1 mole of cyclopentane has larger entropy than that of 1 mole of 1-pentene.
- (B) At 1 bar and 300 K, 1 mole of  $N_2(g)$  in a rectangle box has a much larger entropy than that of  $N_2(g)$  in a cubic box.
- (C) The heat capacity for monoatomic atom F is considerably larger than that for Ne even though they have about same atomic weight.
- (D)  $Br_2(g)$  has a smaller molar heat capacity than that of  $N_2(g)$ .
- (E) The heat capacity of liquid water is much larger than that of water vapor.

17. For the van der Waals equation:  $(P + \frac{n^2 a}{V^2})(V - nb) = nRT$ , which of the following statements is TRUE?

- (A) The term  $\frac{a}{V^2}$  is introduced to correct for the effects of repulsive forces between molecules.
- (B) The term  $nb$  is introduced to correct for the volume occupied by the molecules themselves.
- (C) Among Ar,  $CO_2$ , and He gases, the  $CO_2$  has the largest “a” value.
- (D) For hard-sphere molecules, the “b” value is  $\approx 8V_{\text{molecule}}N_A$  ( $V_{\text{molecule}}$  is the volume per molecule and  $N_A$  is the Avogadro constant).
- (E). The van der Waals equation is applicable for all real gases at all conditions.

※選擇題請在答案卡內作答，非選擇題請在答案卷內作答

18. Sulfur exists in two solid forms, rhombic (**R**) and monoclinic (**M**). Its phase diagram is shown as:



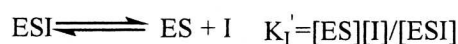
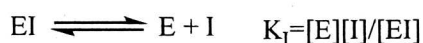
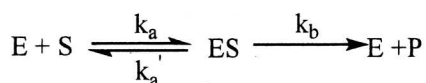
Which of the following statements is TRUE?

- (A) The phase diagram of sulfur has two triplet points.
- (B)  $\frac{\Delta V}{\Delta H}$  is negative for the conversion Rhombic  $\rightarrow$  Monoclinic.
- (C)  $\frac{\Delta V}{\Delta H}$  is zero for the conversion Rhombic  $\rightarrow$  Monoclinic.
- (D) **R** form of sulfur has the higher heat of sublimation than **M** form.
- (E) Rhombic and monoclinic forms of sulfur have same heat of sublimation.
19. For a given material, its vapour pressure  $P$  in atm at absolute temperature  $T$  can be expressed as  $\ln P = 2 - 600/T$  for its solid state and as  $\ln P = 1 - 360/T$  for its liquid state. Assume the external pressure = 1 atm. Which of the following statements is TRUE?
- (A) The  $\ln P$  at the triple point is  $-0.5$ .
- (B) The temperature at the triple point is 240 K.
- (C) The enthalpy of sublimation 4988.4 J/mol.
- (D) The entropy of sublimation is 16.6 J/K-mol.
- (E) The normal boiling point is 360 K.

※選擇題請在答案卡內作答，非選擇題請在答案卷內作答

20. Which of the following statements about Maxwell-Boltzmann distribution is TRUE?
- (A) When the temperature is decreased, the distribution of molecular speeds will become broader and flatter.
- (B) For an isolated system, the integration of the Maxwell-Boltzmann distribution of speed over the speed range of zero and infinity is temperature dependent.
- (C) The value of the most probable velocity  $v_x$  is  $(\frac{2kT}{m})^{1/2}$ .
- (D)  $\langle v_x \rangle^2$  is not equal to  $\langle v_x^2 \rangle$ .
- (E) Generally, the Maxwell-Boltzmann distribution can be validated by the stopped flow technique.

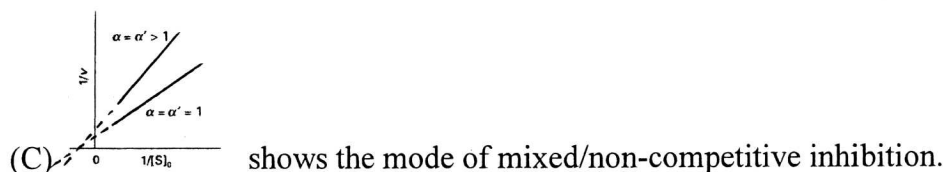
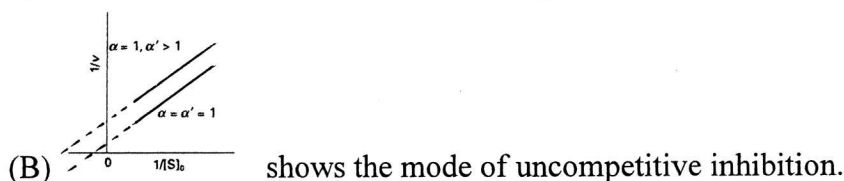
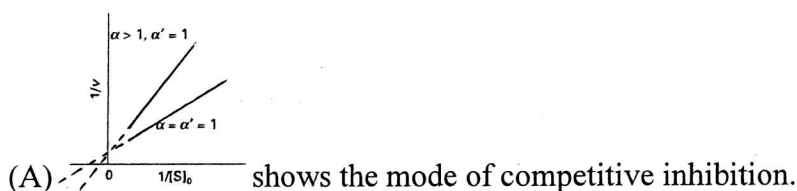
21. The mechanisms of enzyme (E) inhibition are expressed as



,where **I** is the inhibitor and **S** is the substrate. The rate of reaction is

$$v = \frac{v_{\max}}{\alpha' + \alpha K_m / [S]_0} \cdot K_m = \frac{k_a' + k_b}{k_a}, \alpha = 1 + \frac{[I]}{K_I} \text{ and } \alpha' = 1 + \frac{[I]}{K_I'}$$

following statements is TRUE?



- (D) When  $\alpha = \alpha' = 1$ , the result is the same as the Lineweaver-Burke equation.
- (E) The rate of reaction shown above can be validated by stopped flow techniques.

類組：化學類 科目：物理化學(1004)

共 10 頁 第 8 頁

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22. Which of the following thermodynamics equations is TRUE?

(A)  $\left(\frac{\partial H}{\partial P}\right)_T = V - \left(\frac{\partial V}{\partial T}\right)_P$

(B)  $\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial H}{\partial V}\right)_P - 1\right]$

(C)  $\left(\frac{\partial G}{\partial P}\right)_T = V$

(D)  $\left(\frac{\partial G}{\partial T}\right)_P = S$

(E)  $\left(\frac{\partial U}{\partial V}\right)_T = \frac{n^2 a}{V^2}$  for an Van der Waals gas,  $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$ .

23. Which of the following statements is TRUE?

- (A) The value of equilibrium constant is dependent on temperature.
- (B) During a phase transition, the temperature of a substance must be constant.
- (C)  $\Delta S_{\text{mix}} = 0$  after mixing two ideal solutions.
- (D) Inter-molecular interactions are always negligible (close to zero) in an ideal solution.
- (E) If a solute partly dimerizes in a solvent, the freezing point depression is less than it would be if the solute does not dimerize.

注意：背面有試題



※選擇題請在答案卡內作答，非選擇題請在答案卷內作答

二. 計算題 請詳列計算過程，無計算過程者不予計分。

1. (6 分)

(a) Calculate the value of the commutator,  $\left[\frac{d}{dx}, \frac{d}{dx} + x^2\right]$

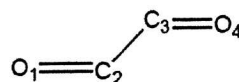
(b) True/False: If two operators commute with a third, they will commute with each other.

(c) Is the operator,  $i^2 \frac{d^2}{dx^2}$  Hermitian?

2. (10 分) Consider a particle in a two dimensional box of length  $\frac{1}{2}b$  in the x direction and b in the y direction; i.e. the dimensions are:  $\frac{1}{2}b \times b$

(a) Draw a diagram containing the lowest 6 energy levels\* of a particle in a two dimensional box of dimensions  $\frac{1}{2}b \times b$ . Put the energies in units of  $h^2/8mb^2$ , and give the degeneracy of each level. (\*Note: A doubly degenerate level would count as only 1 of the 6 levels)

(b) The 10 electrons in naphthalene can be treated as particles in a two dimensional box of dimensions  $\frac{1}{2}b \times b$ , where  $b = 8 \text{ \AA}$ . Use your diagram above to calculate the wavelength, in  $\text{Å}$ , of the lowest energy  $\pi \rightarrow \pi^*$  electronic transition in naphthalene.



3. (6 分) Consider the molecule, ethanedial (right)

The oxygen Hückel parameters are:  $\alpha_o = \alpha + \beta$  and  $\beta_o = 0.8\beta$ . Write the

Secular Determinant in terms of (i)  $\alpha$ ,  $\beta$  and E, (ii)  $x = \left(\frac{\alpha - E}{\beta}\right)$

類組：化學類 科目：物理化學(1004)

共 10 頁 第 10 頁

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4. (8 分) Consider the three CH bending vibrations of (E)-1,2-dichloroethene, which belongs to the  $C_{2h}$  point group.

 **$C_{2h}$  Character Table**

$C_{2h}$	E	$C_2$	i	$\sigma_h$	
$A_g$	1	1	1	1	$x^2, y^2, z^2, xy$
$B_g$	1	-1	1	-1	$xz, yz$
$A_u$	1	1	-1	-1	$z$
$B_u$	1	-1	-1	1	$x, y$

The vibrations modes (and symmetries) are:

$$\nu_1 \sim = 900 \text{ cm}^{-1} (a_u) \quad \nu_2 \sim = 760 \text{ cm}^{-1} (b_g) \quad \nu_3 \sim = 1200 \text{ cm}^{-1} (b_u)$$

Consider the combination mode,  $(0,1,0) \rightarrow (1,0,2)$   $[(\nu_1, \nu_2, \nu_3)]$ . Determine whether this combination mode is (i) IR active AND/OR (ii) Raman active.