

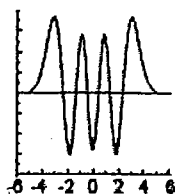
The following symbols have the specified definitions unless they are noted in the questions.

$T$ = temperature	$n$ = number of moles
$P$ = pressure	$C_P$ = heat capacity at constant pressure
$V$ = volume	$C_V$ = heat capacity at constant volume
$U$ = internal energy	$R$ = molar gas constant
$H$ = enthalpy	= 8.314 joules/(mol · K)
$S$ = entropy	= 0.0821 L · atm/(mol · K)
$G$ = Gibbs free energy	$k$ = rate constant
	$k_B$ = Boltzmann constant
	= $0.695 \text{ cm}^{-1} \cdot \text{K}^{-1}$

一. 選擇題 (選擇題答案請填於答案卡)

(一) 單選題，每題 3 分，共 60 分。每題 5 個選項，其中只有一個是最適當的答案，答對才給分；答錯每題倒扣 0.75 分，倒扣至本大題(即單選題)零分為止。

- According to Marcus theory, which of the following factor does NOT influence the electron transfer rate constant?
  - Reorganization energy.
  - Gibbs energy difference between the product and reactant.
  - Angular momentum of electron
  - Distance between electron donor and acceptor.
  - Type of spacer between electron donor and acceptor.
- The energy levels of the linear harmonic oscillator are
  - all nondegenerate
  - $n$ -fold degenerate
  - $(n + 1/2)$ -fold degenerate
  - $(2n + 1)$ -fold degenerate
  - $n^2$ -fold degenerate
- The illustrated wave function represents the state of the linear harmonic oscillator



with  $n =$  (A) 2 (B) 3 (C) 4 (D) 5 (E) 6

4. There is one state at  $\epsilon = 0$  and there are two states at  $\epsilon = 300 \text{ cm}^{-1}$ . According to the Boltzmann distribution, the population of second state is 0.15. What is the temperature (K)?
- (A) 180 K  
(B) 300K  
(C) 480 K  
(D) 90 K  
(E) > 1000 K
5. The rate constant of a chemical reaction is NOT determined by
- (A) steric requirement  
(B) encounter rate  
(C) minimum energy requirement  
(D) temperature  
(E) standard reaction free energy
6. Spherical polar coordinates are used in the solution of the hydrogen atom Schrodinger equation because
- (A) the Laplacian operator has its simplest form in spherical polar coordinates.  
(B) Cartesian coordinates would give particle-in-a-box wave functions.  
(C) the Schrodinger equation is then separable into 3 ordinary differential equations.  
(D) Otherwise the atomic orbitals would violate the Pauli Exclusion Principle.  
(E) Schrodinger first used this coordinate system; any other coordinate system would be equally convenient.
7. 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  $0.02 \text{ sec}^{-1}$ . After initiation of the reaction, at what time would you expect the pressure to be 2.0 atm?
- (A) 693 sec  
(B) 34.65 sec  
(C) 263 sec  
(D) 699 sec  
(E) Can not be determined.
8. Molecules are known to absorb radiation in which region of the electromagnetic spectrum:
- (A) Ultraviolet (B) visible (C) infrared (D) microwave (E) all of the above

9. The van der Waals equation is expressed as  $(P + \frac{n^2a}{V^2})(V - nb) = nRT$ . Which of the following statement is true?
- (A) Compression factor  $Z < 1$  when  $a/(RT) > b$ .  
 (B) Compression factor  $Z < 1$  when  $a/(RT) < b$ .  
 (C) Compression factor  $Z < 1$  when  $a/(RT^2) < b$ .  
 (D) Compression factor  $Z < 1$  when  $a < b/(RT)$ .  
 (E) All of the above is incorrect.
10. Which of the following is "NOT" a correct aspect of the Born-Oppenheimer approximation
- (A) The electrons in a molecule move much faster than the nuclei.  
 (B) Excited electronic states have the same equilibrium inter-nuclear distance as the ground electronic state.  
 (C) The electronic and vibrational motions of a molecule are approximately separable.  
 (D) Electronic energy curves serve as potential energy functions for nuclear vibrational 3 motions.  
 (E) The typical amplitude of nuclear vibration is much smaller than that characterizing the motion of electrons.
11. The benzene molecule  $C_6H_6$  has how many vibrational modes
- (A) 6 (B) 12 (C) 24 (D) 30 (E) 36
12. For the reaction  $A + B \rightarrow \text{product}$ , the reaction rate is first order to A and first order to B. Integrate the rate law.  $[A]_0$  and  $[B]_0$  are the initial concentrations for A and B, respectively and  $[A]_0$  is not equal to  $[B]_0$ .  $t = \text{time}$ .
- (A)  $kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A]_0[B]}{[A][B]_0}$   
 (B)  $kt = \frac{-1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[A]_0[B]}$   
 (C)  $kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]}{[A]_0[B]_0}$   
 (D)  $kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[A]_0[B]}$   
 (E) All of the above is incorrect.

13. The normal boiling temperature of ethanol is  $78.5^{\circ}\text{C}$  and its molar enthalpy change of vaporization at this temperature is  $40.3\text{ kJ/mol}$ . Find  $\Delta U$  when  $3.000\text{ mol}$  of ethanol are vaporized at  $78.5^{\circ}\text{C}$  at a constant pressure of  $1.000\text{ atm}$ . Neglect the volume of the liquid compared with that of the vapor and assume the ethanol vapor as an ideal gas.
- (A)  $\Delta U = 120.9\text{ kJ}$   
(B)  $\Delta U = 0.0\text{ kJ}$   
(C)  $\Delta U = -8.77\text{ kJ}$   
(D)  $\Delta U = 130.1\text{ kJ}$   
(E)  $\Delta U = 112.1\text{ kJ}$
14. The ionization energy for hydrogen atom is  $13.6\text{ eV}$ . The ionization Energy for the ground state of  $\text{Li}^{2+}$  is approximately
- (A) 13.6 (B) 27.2 (C) 40.8 (D) 54.4 (E) 122.4 eV
15. 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.
16. The Joule coefficient,  $\mu_J$ , is defined as  $\mu_J = (\partial T/\partial V)_U$ .  $\alpha$  is the thermal expansion coefficient.  $\kappa_T$  is the isothermal compressibility. Which of the following equation is correct?
- (A)  $\mu_J C_V = p + \alpha T/\kappa_T$   
(B)  $\mu_J C_V = p - \alpha T/\kappa_T$   
(C)  $\mu_J C_V = p + \kappa_T T/\alpha$   
(D)  $\mu_J C_V = p - \kappa_T T/\alpha$   
(E)  $\mu_J C_V = \alpha T/\kappa_T$
17. The orbital degeneracy (excluding spin) of hydrogen atom energy levels equals
- (A)  $n-1$  (B)  $n$  (C)  $n+1$  (D)  $2n+1$  (E)  $n^2$

18. The change in enthalpy is given by  $dH = C_p dT + V dp$ . In combination with the Clapeyron equation, find out  $d(\Delta H/T)$  and the two phases remain in equilibrium.

- (A)  $d(\Delta H/T) = \Delta C_p d(\ln T)$
- (B)  $d(\Delta H/T) = R d(\ln T)$
- (C)  $d(\Delta H/T) = \Delta S d(\ln T)$
- (D)  $d(\Delta H/T) = C_p d(\ln T)$
- (E) All of the above is incorrect

19. 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 plank constant,  $h$ .
- (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.

20. At the solid-liquid-vapor triple point of a pure substance, what is the slope,  $dp/dT$  of phase transition?

- (A) solid-vapor line  $>$  liquid-vapor line
- (B) solid-vapor line = liquid-vapor line
- (C) solid-vapor line  $<$  liquid-vapor line
- (D) solid-vapor line = liquid-vapor line = 0
- (E) all of the above is incorrect

(二) 多選題，每題 5 分，共 15 分。每題有 5 個選項，每答對一個選項，可得 1 分；每答錯一個選項，倒扣 1 分；未作答者，該題以零分計算；倒扣至本大題(即多選題)零分為止。

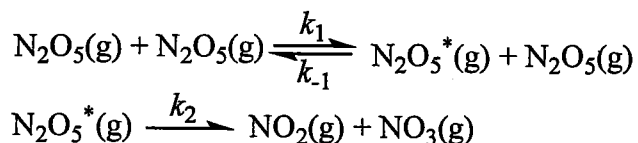
21. Based on statistical thermodynamics, which of the following statement about heat capacity is true?

- (A) The  $C_p$  for Ar is the same as that for Ne, even though the atomic weight of Ar is twice that of Ne.
- (B) The heat capacity for monoatomic atom F is considerably larger than that for Ne even though they have about same atomic weight.
- (C) The heat capacity of liquid water is much larger than that of water vapor.
- (D)  $\text{Br}_2(\text{g})$  has larger  $C_p$  value than that of  $\text{Cl}_2(\text{g})$ .
- (E) The  $C_p$  values for the Ar,  $\text{O}_2(\text{g})$ , and  $\text{Cl}_2(\text{g})$  are in the order of  $\text{Cl}_2(\text{g}) > \text{O}_2(\text{g}) > \text{Ar}$ .

注意：背面有試題

22. The velocity probability of Maxwell-Boltzmann distribution in one-direction is expressed as:  $f(v_x) = k' e^{-mv_x^2/2kT}$ . Which of the following statement about Maxwell-Boltzmann distribution at a finite T is true?
- (A) The most-probable velocity for a one-dimensional gas velocity distribution is zero.
- (B) The Maxwell-Boltzmann speed (three dimensions) distribution approaches zero at high speeds.
- (C) The Maxwell-Boltzmann speed (three dimensions) distribution approaches zero at low speed.
- (D) The total energy of one mole perfect gas according to the Maxwell-Boltzmann distribution is 1.5RT.
- (E) Most-probable speed > Mean speed > Root mean square speed.

23. Consider the collision-induced dissociation of  $N_2O_5(g)$  via the following mechanism:



The \* symbol in the first reaction indicates the reactant is activated through collision. Experimentally, it is observed that the reaction can be either first or second order under different conditions. The rate law is expressed as  $R = \frac{k[N_2O_5]^m}{1+k'[N_2O_5]}$ . Which

of the following statement is true?

- (A)  $m = 2$ .
- (B)  $k' = k_1$
- (C)  $k' = k_{-1} / k_2$
- (D) When  $k_{-1}[N_2O_5] \gg k_2$ , the reaction will be first order in  $N_2O_5(g)$ .
- (E) When  $k_{-1}[N_2O_5] \ll k_2$ , the reaction will be half order in  $N_2O_5(g)$ .

二. 計算題，共 25 分。作答時請清楚標示題號、詳列計算過程、並將最後答案標示清楚。

1. (5 pts) Assume the molar Gibbs free energy of a gas is given by the equation:

$$G_m - RT \ln\left(\frac{P}{p_0}\right) + (a + bT)P = 0, \text{ where } p_0 \text{ is the standard pressure and } a \text{ and}$$

$b$  are gas-dependent constants. Derive an equation of state for this gas. Show the final result in the form of  $PV = ?$ .

2. (10 pts) The bonding in Hydrogen Iodide (HI) can be described by a two orbital interaction between the  $1s$  orbital on Hydrogen and the  $5p$  orbital on Iodine. The Hamiltonian matrix elements (coulomb integrals, exchange integral and overlap integral) are:  $H_{HH} = -14 \text{ eV}$   $H_{II} = -10 \text{ eV}$   $H_{HI} = -3 \text{ eV}$   $S_{HI} = 0 \text{ eV}$

Assume that the molecular wave function is:

$$\psi = c_H 1s_H + c_I 5p_I$$

- a) (4pts) Set up the Secular Determinant and solve for the energy of the Bonding and Anti-Bonding Orbitals
- b) (4pts) Use your answer in part (a) to calculate the coefficients,  $C_H$  and  $C_I$ , in the **Normalized anti-bonding** orbital. If you are not sure of the energy, then use  $E_{\text{antibond}} = -8.0 \text{ eV}$  to work out this part.
- c) (2pts) Assume for this part that the bonding orbital is:

$$\psi = N[(0.5) \cdot 1s_H + (0.9) \cdot 5p_I]$$

What fraction of the charge of an electron in the bonding orbital is on the Iodine atom?

3. (10 pts) Consider a transition between the ground state ( $\Psi_0$ ) and the  $i$ 'th excited state ( $\Psi_i$ ). Time dependent perturbation theory can be used to show that the intensity of the absorption is proportional to the square of the "transition moment",  $M_{0i}$ . The x, y and z components of the transition moment are: .

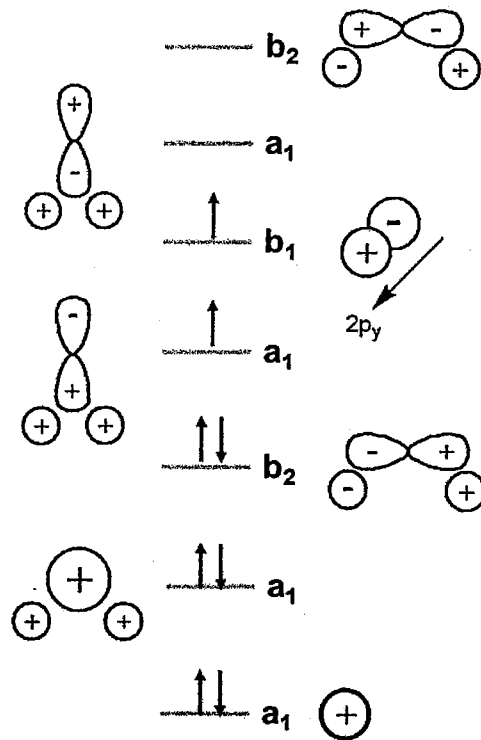
$$M_{0i}^x = e \langle \Psi_i | x | \Psi_0 \rangle$$

$$M_{0i}^y = e \langle \Psi_i | y | \Psi_0 \rangle$$

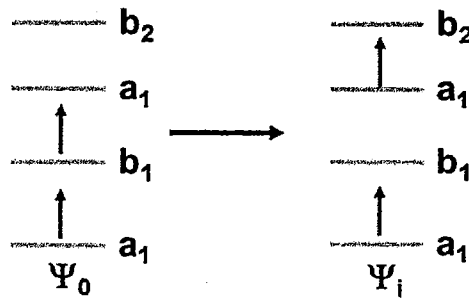
$$M_{0i}^z = e \langle \Psi_i | z | \Psi_0 \rangle$$

In the case of **Carbene**, it has  $C_{2v}$  symmetry has 8 electrons and the Triplet Ground state takes the electronic configuration  $(a_1)^2(a_1)^2(b_2)^2(a_1)^1(a_1)^1$  as shown in the following diagram where the shape of the molecular orbital are also included

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Please determine if the electronic transition (only the highest two unpaired electrons are shown and the paired inner orbitals are neglected) is UV allowed or forbidden.



For your information, the character table for  $C_{2v}$  symmetry is:

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$	
$A_1$	1	1	1	1	Z
$A_2$	1	1	-1	-1	
$B_1$	1	-1	1	-1	X
$B_2$	1	-1	-1	1	Y