

※選擇題請在答案卡內作答，非選擇題請在答案卷內作答

1-10 題為單選題，每題三分，採電腦閱卷，請用答案卡作答，答錯不倒扣：

List of abbreviations:

$U$ : internal energy,  $H$ : enthalpy,  $S$ : entropy,

$G$ : Gibbs free energy,  $A$ : Helmholtz free energy,  $\mu$ : chemical potential,

$q$ : heat,  $w$ : work;  $P$ : pressure,  $V$ : volume,  $T$ : temperature,  $R$ : gas constant

$C_{v,m}$ : constant-volume molar heat capacity,

$C_{p,m}$ : constant-pressure molar heat capacity,

$\pi_T$ : internal pressure

- Which of the following equations is correct? (A)  $H = U + TS$ , (B)  $A = U - PV$ , (C)  $G = H + TS$ , (D)  $C_{p,m} - C_{v,m} = \frac{1}{2}R$  for a perfect gas, (E) none of the above.
- Which of the following equations is correct? (A)  $C_v = \left(\frac{\partial H}{\partial T}\right)_v$ , (B)  $\pi_T = \left(\frac{\partial H}{\partial V}\right)_T$ , (C)  $-S = \left(\frac{\partial A}{\partial T}\right)_p$ , (D)  $-P = \left(\frac{\partial A}{\partial p}\right)_T$ , (E)  $dS \geq \frac{dq}{T}$ .
- A sample consisting of 1.00 mole of He(g) is expanded isothermally at  $T = 273 \text{ K}$  from  $20.0 \text{ dm}^3$  to  $40.0 \text{ dm}^3$  against a constant external pressure equal to the final pressure of the gas. What are the  $q$ ,  $w$  and  $\Delta U$  of the process?  
 (A)  $q = 1.13 \text{ kJ}$ ,  $w = -2.26 \text{ kJ}$  and  $\Delta U = -1.13 \text{ kJ}$ .  
 (B)  $q = 1.13 \text{ kJ}$ ,  $w = -1.13 \text{ kJ}$  and  $\Delta U = 0 \text{ kJ}$ .  
 (C)  $q = -1.13 \text{ kJ}$ ,  $w = -2.26 \text{ kJ}$  and  $\Delta U = -3.39 \text{ kJ}$ .  
 (D)  $q = 0 \text{ kJ}$ ,  $w = -1.13 \text{ kJ}$  and  $\Delta U = -1.13 \text{ kJ}$ .  
 (E)  $q = 1.13 \text{ kJ}$ ,  $w = 0 \text{ kJ}$  and  $\Delta U = 1.13 \text{ kJ}$ .
- About the Carnot cycle of a perfect gas, which of the following statements is true?  
 (A) The  $U$  of the system decreases, because there is work output in a Carnot cycle.  
 (B) The perfect gas follows  $PV = \text{constant}$  in the whole Carnot cycle.  
 (C) The  $S$  of the system does not change after a complete Carnot cycle.  
 (D) The perfect gas goes through the Carnot cycle spontaneously.  
 (E) An engine running with the Carnot cycle has engine efficiency of 100%.
- If  $H_2(g)$  is compressed from  $160 \text{ m}^3$  at  $400 \text{ K}$  to  $40 \text{ m}^3$  at  $200 \text{ K}$ , what is the value of  $\Delta S_m$ ?  
 Take  $C_{p,m} = 29.4 \text{ JK}^{-1}\text{mol}^{-1}$ ,  $\ln(2) = 0.69$ .  
 (A)  $26 \text{ JK}^{-1}\text{mol}^{-1}$ , (B)  $-32 \text{ JK}^{-1}\text{mol}^{-1}$ , (C)  $-26 \text{ JK}^{-1}\text{mol}^{-1}$ , (D)  $13 \text{ JK}^{-1}\text{mol}^{-1}$ , (E)  $32 \text{ JK}^{-1}\text{mol}^{-1}$ .

參考用

注意：背面有試題

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6. About free energy, which of the following statement is true.
- (A) At constant  $P$ , Gibbs free energy increase with  $T$ .  
 (B) At constant  $T$ , Helmholtz free energy increase with  $P$ .  
 (C) As a system approaches equilibrium, the second derivatives of free energy approaches zero.  
 (D) At constant temperature and pressure, the maximum non-expansion work can be expressed by  $dw = dG$ .  
 (E) At a given temperature, a chemical reaction involving a more negative  $\Delta_r G$  will have a lower equilibrium constant than a reaction that has a less negative  $\Delta_r G$ .
7. The molar enthalpy of vaporization ( $\Delta_{vap}H_m$ ) of benzene at its normal boiling point ( $80.09^\circ\text{C}$ ) is  $30.72 \text{ kJ mol}^{-1}$ . What are the value of the molar Gibbs free energy of vaporization ( $\Delta_{vap}G_m$ ) and the value of molar entropy of vaporization ( $\Delta_{vap}S_m$ ) at  $80.09^\circ\text{C}$ ?
- (A)  $\Delta_{vap}G_m = 0.4411 \text{ kJ mol}^{-1}$ ,  $\Delta_{vap}S_m = 58.72 \text{ JK}^{-1}\text{mol}^{-1}$ .  
 (B)  $\Delta_{vap}G_m = 0$ ,  $\Delta_{vap}S_m = 86.97 \text{ JK}^{-1}\text{mol}^{-1}$ .  
 (C)  $\Delta_{vap}G_m = 0$ ,  $\Delta_{vap}S_m = 383.6 \text{ JK}^{-1}\text{mol}^{-1}$ .  
 (D)  $\Delta_{vap}G_m = -0.4411 \text{ kJ mol}^{-1}$ ,  $\Delta_{vap}S_m = 88.22 \text{ JK}^{-1}\text{mol}^{-1}$ .  
 (E) none of the above.
8. The rate constant of a reaction increases 100 times from  $T = 200 \text{ K}$  to  $400 \text{ K}$ . What is the activation energy of the reaction. Take  $\ln(10) = 2.30$ .
- (A)  $12.4 \text{ kJ mol}^{-1}$ , (B)  $15.3 \text{ kJ mol}^{-1}$ , (C)  $24.8 \text{ kJ mol}^{-1}$ , (D)  $30.6 \text{ kJ mol}^{-1}$ , (E)  $6.2 \text{ kJ mol}^{-1}$ .
9. At  $T = 298 \text{ K}$  and  $P = 1.33 \times 10^{-7} \text{ Pa}$ , a gas sample consists of  $\text{N}_2$  molecules with a collision diameter of  $395 \text{ pm}$ . What are the mean speed ( $v_{mean}$ ) of the molecules, and the mean free path ( $\lambda$ ) in the gas?
- (A)  $v_{mean} = 475 \text{ ms}^{-1}$ ,  $\lambda = 6.31 \times 10^4 \text{ m}$ .  
 (B)  $v_{mean} = 525 \text{ ms}^{-1}$ ,  $\lambda = 4.32 \times 10^4 \text{ m}$ .  
 (C)  $v_{mean} = 830 \text{ ms}^{-1}$ ,  $\lambda = 5.62 \times 10^4 \text{ m}$ .  
 (D)  $v_{mean} = 232 \text{ ms}^{-1}$ ,  $\lambda = 8.57 \times 10^4 \text{ m}$ .  
 (E)  $v_{mean} = 371 \text{ ms}^{-1}$ ,  $\lambda = 9.35 \times 10^4 \text{ m}$ .

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10. Regarding an ideal solution of A(l) and B(l), which of the following statements is true?
- (A) Adding B(l) into pure A(l) increases the chemical potential of A(l).
- (B) The mixing process of A(l) and B(l) is spontaneous because the entropy of mixing ( $\Delta_{mix}S$ ) is negative.
- (C) The composition in the gas phase is richer in A, if the vapor pressure of pure A(l) is equal to the vapor pressure of pure B(l).
- (D) The enthalpy of mixing ( $\Delta_{mix}H$ ) has no contribution to the mixing process.
- (E) The activity of A(l) is higher than the mole fraction of A(l).

11-14 題為多選題，每題五分，採電腦閱卷，請用答案卡作答，每一選項的個別分數為一分，答錯的選項倒扣一分：

11.  $\theta_R$  is the characteristic rotational temperature,  $\theta_V$  is the characteristic vibrational temperature, and  $C_{v,m}$  is the molar heat capacity at constant volume. Assume that a perfect gas of diatomic molecules has  $\theta_R = 60\text{ K}$  and  $\theta_V = 273\text{ K}$ , which of the following statements about  $C_{v,m}$  are true?

The  $C_{v,m}$  of the diatomic molecule is

- (A)  $8.314\text{ J K}^{-1}\text{ mol}^{-1}$  at  $T = 40\text{ K}$ ,
- (B)  $29.1\text{ J K}^{-1}\text{ mol}^{-1}$  at  $T = 300\text{ K}$ ,
- (C)  $20.8\text{ J K}^{-1}\text{ mol}^{-1}$  at  $T = 40\text{ K}$ ,
- (D)  $12.5\text{ J K}^{-1}\text{ mol}^{-1}$  at  $T = 150\text{ K}$ ,
- (E)  $20.8\text{ J K}^{-1}\text{ mol}^{-1}$  at  $T = 100\text{ K}$ .

12. A pure substance has a boiling point of  $T_b$ , and a melting point of  $T_m$  at a pressure in-between the triple point pressure ( $p_3$ ) and the critical point pressure ( $p_c$ ) of the substance. Which of the following statements about the  $\mu - T$  plot of the substance are true?
- (A) At  $T > T_b$ , the  $\mu$  of the vapor phase is lower than the  $\mu$  of the solid phase.
- (B) The solid phase has the lowest  $\mu$  at  $T < T_m$ .
- (C) At  $T = T_m$ , the liquid phase and the vapor phase have identical  $\mu$ .
- (D) The liquid phase is the most stable state at  $T_m < T < T_b$ .
- (E) the solid phase gives a  $\mu - T$  curve with a less negative slope than the gas phase, because the solid phase has a smaller molar volume.

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類組：化學類 科目：物理化學(1004)

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13. Which of the following statements are true?

- (A) Gases that have Joule-Thomson coefficient larger than zero, show heating effect on expansion.
- (B) Repulsive intermolecular interactions are dominating in gases with compression factor less than 1.
- (C) In Joule free expansion, the internal energy of gas molecules increases as the volume of the gas increase, if the internal pressure of the gas is positive.
- (D) In Joule-Thomson expansion, the enthalpy of the system is a constant.
- (E) If the mixing of two liquids ( $A(l)$  and  $B(l)$ ) is exothermic, the A-B interactions are more favorable than the A-A and B-B interactions.

14. In the reaction  $A+2B\rightarrow 3C+4D$ , the rate of consuming B is  $4.0 \text{ mol dm}^{-3}\text{s}^{-1}$ , and the rate law for the reaction was found to be  $R = k[A][B]^2$ . Which of the following statements are correct?

- (A) The rate of formation of C is  $6.0 \text{ mol dm}^{-3}\text{s}^{-1}$ .
- (B) The unit of the rate constant  $k$  is  $\text{dm}^6\text{mol}^{-2}\text{s}^{-1}$ .
- (C) The reaction is a second-order reaction.
- (D) If the reaction is exothermic, the equilibrium constant of the reaction decreases as the temperature rises.
- (E) The rate of consumption of A is  $4.0 \text{ mol dm}^{-3}\text{s}^{-1}$ .

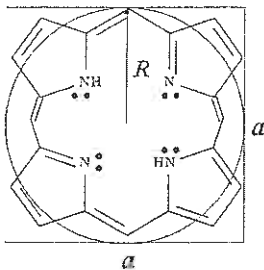
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15-17 題為計算題： • 計算題應詳列計算過程，無計算過程者不給分。

15. (20 分) Consider porphyrin molecule that has 26  $\pi$  electrons as planar geometry in the following figure. All  $\pi$  electrons are confined inside the plane. Using the 2D-box model with  $a=1000\text{pm}$  ( $1\text{pm}=10^{-12}\text{m}$ ), to calculate the lowest energy absorption of the porphyrin molecule (the experiment value is  $=17000\text{cm}^{-1}$ ).



Hint  $\left( E_{n_x n_y} = \frac{h^2}{8ma^2} [n_x^2 + n_y^2] \right)$ ,  $m = 9.1 \times 10^{-31} \text{kg}$ ,  $\hbar = 1.1 \times 10^{-34} \text{J} \cdot \text{s}$ ,  $h = 2\pi\hbar$ ,  $\pi = 3.14$

16. (10 分) The highest occupied molecular orbitals for excited-state oxygen molecule are

$(1\pi_g)^1 (3\sigma_u)^1$ , determine the term symbols and energy order of terms (by Hund's rule).

17. (20 分) An oscillator particle has Hamiltonian  $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + cx^4$  where  $-\infty < x < \infty$ , use trial

function  $\psi(x) = e^{-\beta x^2}$  to calculate (by variation method)

$$E(\beta) = \frac{\int_{-\infty}^{\infty} \psi(x) \hat{H} \psi(x) dx}{\int_{-\infty}^{\infty} \psi(x) \psi(x) dx} \quad \text{and then} \quad \frac{\partial E(\beta)}{\partial \beta} = 0$$

(Hint:  $I_n = \int_{-\infty}^{\infty} x^{2n} e^{-\beta x^2} dx = \frac{(2n-1)!}{(2\beta)^n} \sqrt{\frac{\pi}{\beta}}$ )

參考用