

※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, μ : 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,

π_T : internal pressure

1. 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.

2. 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) $dS \geq \frac{dq}{T}$.

3. A sample consisting of 1.00 mole of He(g) is expanded isothermally at $T = 273$ K from 20.0 dm³ to 40.0 dm³ against a constant external pressure equal to the final pressure of the gas. What are the q , w and ΔU of the process?

(A) $q = 1.13$ kJ, $w = -2.26$ kJ and $\Delta U = -1.13$ kJ.

(B) $q = 1.13$ kJ, $w = -1.13$ kJ and $\Delta U = 0$ kJ.

(C) $q = -1.13$ kJ, $w = -2.26$ kJ and $\Delta U = -3.39$ kJ.

(D) $q = 0$ kJ, $w = -1.13$ kJ and $\Delta U = -1.13$ kJ.

(E) $q = 1.13$ kJ, $w = 0$ kJ and $\Delta U = 1.13$ kJ.

4. 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%.

5. If $H_2(g)$ is compressed from 160 m³ at 400 K to 40 m³ at 200 K, what is the value of ΔS_m ?

Take $C_{p,m} = 29.4$ JK⁻¹mol⁻¹, $\ln(2) = 0.69$.

(A) 26 JK⁻¹mol⁻¹, (B) -32 JK⁻¹mol⁻¹, (C) -26 JK⁻¹mol⁻¹, (D) 13 JK⁻¹mol⁻¹, (E)

32 JK⁻¹mol⁻¹.

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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°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°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 K . What is the activation energy of the reaction. Take $\ln(10) = 2.30$.
- (A) 12.4 kJ mol^{-1} , (B) 15.3 kJ mol^{-1} , (C) 24.8 kJ mol^{-1} , (D) 30.6 kJ mol^{-1} , (E) 6.2 kJ mol^{-1} .
9. At $T = 298 \text{ K}$ and $P = 1.33 \times 10^{-7} \text{ Pa}$, a gas sample consists of N_2 molecules with a collision diameter of 395 pm . What are the mean speed (v_{mean}) of the molecules, and the mean free path(λ) 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. θ_R is the characteristic rotational temperature, θ_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 μ of the vapor phase is lower than the μ of the solid phase.
- (B) The solid phase has the lowest μ at $T < T_m$.
- (C) At $T = T_m$, the liquid phase and the vapor phase have identical μ .
- (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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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 $4.0 \text{ mol dm}^{-3}\text{s}^{-1}$.

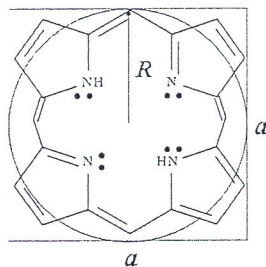
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15-17 題為計算題： • 計算題應詳列計算過程，無計算過程者不給分。

15. (20 分) Consider porphyrin molecule that has 26 π electrons as planar geometry in the following figure. All π 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: $I_n = \int_{-\infty}^{\infty} x^{2n} e^{-\beta x^2} dx = \frac{(2n-1)!!}{(2a)^n} \sqrt{\frac{\pi}{\beta}}$)

參考用

