

※選擇題請在答案卡內作答，非選擇題請在答案卷內作答

一、多選題 (每題 5 分，共 40 分，每題單一選項答錯倒扣 1 分)

Symbols and constants for 一及二

P : pressure; V : volume; T : temperature; U : internal energy; H : enthalpy; S : entropy; G : Gibbs energy; q : heat; w : work; C : heat capacity; μ : chemical potential; k : rate constant; \bar{X} : molar property X (example \bar{S} : molar entropy)

Gas constant $R=8.314 \text{ J K}^{-1}\text{mol}^{-1}=8.314\times 10^{-2} \text{ L bar K}^{-1}\text{mol}^{-1}=8.206\times 10^{-2} \text{ L atm K}^{-1}\text{mol}^{-1}$

1. Which of the following statements is/are true?

- (A) For every process in an isolated system, $\Delta T=0$.
- (B) For every process in an isolated system, $\Delta U=0$.
- (C) For every process in an isolated system, $\Delta S=0$.
- (D) $dU=C_V dT$ is always valid even when V is not constant.
- (E) It is possible for the entropy of a closed system to decrease substantially in an irreversible process.

2. Which of the following statements conform(s) with the second law of thermodynamics?

- (A) $dS > dq_{rev} / T$
- (B) $dS = dq_{rev} / T$
- (C) $dS \geq dq / T$
- (D) $dS \leq dq / T$
- (E) $\oint \frac{dq}{T} \leq 0$

3. Consider the reversible melting (fusion) of a pure solid X at the normal melting temperature, which of the following is/are true?

- (A) $\Delta S_X=0$
- (B) $\Delta S_X>0$
- (C) $\Delta S_{total}=0$
- (D) $\Delta S_{total}>0$
- (E) $\Delta S_{surrounding}<0$

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4. Consider a chemical reaction $A+B=C+D$ that is at equilibrium at the extent of reaction $\xi=0.2$ at $P=1$ bar and $T=298.15$ K, which of the following is/are correct?

- (A) the standard reaction Gibbs energy $\Delta_r G^\circ=0$.
 (B) the change of standard Gibbs energy from $\xi=0$ to $\xi=0.2$ is zero, i.e., $\Delta G^\circ(\xi=0.2)=0$.
 (C) $\left(\frac{\partial G}{\partial \xi}\right)_{T,P,\xi=0.2} = 0$
 (D) $\left(\frac{\partial G}{\partial \xi}\right)_{T,P,\xi=0.4} > 0$
 (E) If $\Delta_r G^\circ > 0$, no products (C and D) can be produced.

5. Consider the mixing of one mole of an ideal gas A and one mole of another ideal gas B, which of the following is/are true?

- (A) $\Delta H_{\text{mix}}=0$
 (B) $\Delta S_{\text{mix}} = -2R \ln 2$
 (C) $\Delta S_{\text{mix}} = 2R \ln 2$
 (D) $\Delta G_{\text{mix}} = -2RT \ln 2$
 (E) $\Delta G_{\text{mix}} = 2RT \ln 2$

6. Which of the following is/are true for a closed one-component system of a real gas?

- (A) $dG = -SdT + VdP$
 (B) $\left(\frac{\partial U}{\partial V}\right)_T = 0$
 (C) $\left(\frac{\partial H}{\partial P}\right)_T \neq 0$
 (D) $\bar{C}_P - \bar{C}_V = R$
 (E) $dH = C_p dT$

7. A real gas can be approximately described by an equation of state, $P(\bar{V} - b) = RT$, where \bar{V} is the molar volume and b is a constant. Which of the following is/are true?

- (A) $\left(\frac{\partial \bar{S}}{\partial P}\right)_T = -\frac{R}{\bar{V} - b}$
 (B) $\left(\frac{\partial S}{\partial V}\right)_T = \frac{R}{\bar{V} - b}$
 (C) $\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{\bar{V} - b}$
 (D) $\left(\frac{\partial U}{\partial V}\right)_T = 0$
 (E) $\left(\frac{\partial \bar{H}}{\partial P}\right)_T = b$

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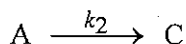
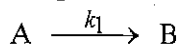
參考用

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8. Consider a parallel reaction mechanism



Given the initial conditions $[A]_0 \neq 0$ and $[B]_0 = [C]_0 = 0$, which of the following is/are correct?

(A) $[A]_t = [A]_0 e^{-k_1 t}$

(B) $[A]_t = [A]_0 e^{-(k_1+k_2)t}$

(C) $[B]_t = \frac{k_1}{k_1+k_2} [A]_0 (1 - e^{-k_1 t})$

(D) $[B]_t = \frac{k_1}{k_1+k_2} [A]_0 (1 - e^{-(k_1+k_2)t})$

(E) $\frac{[B]_t}{[C]_t} = \frac{k_2}{k_1}$

二、單選題 (每題 2 分，共 10 分)

9. Which of the following statements is true?

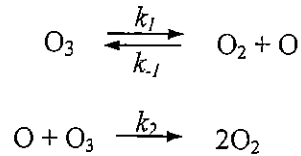
- (A) For a two-component system, the maximum number of phases that can coexist is three.
- (B) For a one-component system, the most stable phase at a given T and P is the phase with the lowest molar Gibbs energy.
- (C) For a simple one-component system, the maximum number of phases that can coexist is three, and the coexisting three phases must be one gas phase, one liquid phase, and one solid phase.
- (D) Three independent intensive variables are required to fully specify the intensive state of a simple three-component system.
- (E) When a binary liquid mixture boils at the azeotrope composition, the partial vapor pressures of the two liquids are the same.

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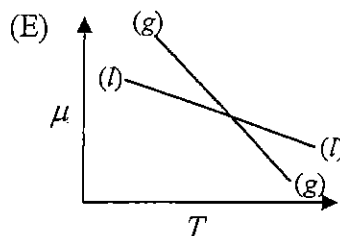
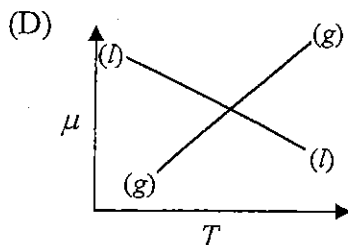
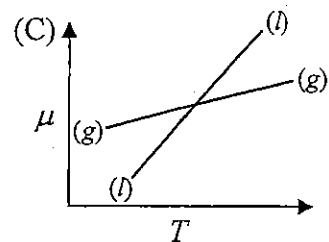
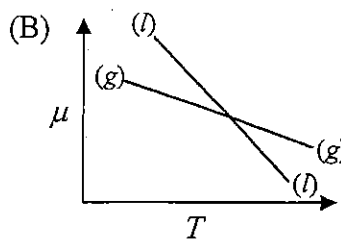
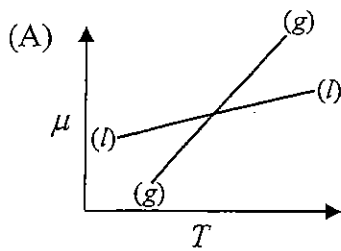
10. The gas-phase decomposition of ozone, $2\text{O}_3 \rightarrow 3\text{O}_2$, is believed to proceed through the mechanism



Which of the following is/are correct on the basis of the steady-state approximation?

- (A) $-\frac{d[\text{O}_3]}{dt} = \frac{2k_1k_2[\text{O}_3]}{k_{-1}[\text{O}_2]}$
- (B) $-\frac{d[\text{O}_3]}{dt} = \frac{2k_1k_2[\text{O}_3]^2}{k_1k_{-1}[\text{O}_2] + k_2k_{-1}[\text{O}_3]}$
- (C) $-\frac{d[\text{O}_3]}{dt} = \frac{2k_1k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]}$
- (D) $-\frac{d[\text{O}_3]}{dt} = \frac{2k_1k_2[\text{O}_3]^2}{k_1k_{-1}[\text{O}_2] + k_2k_{-1}[\text{O}_3]}$
- (E) $-\frac{d[\text{O}_3]}{dt} = \frac{2k_1k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2]}$

11. Which of the following figures displays possible dependences of the chemical potential (μ) on temperature, i.e., $\mu(T)$, of the liquid (l) and gas (g) phases of a pure substance at a constant pressure?

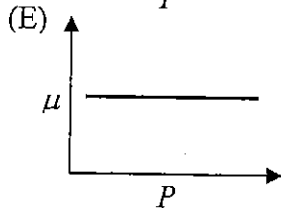
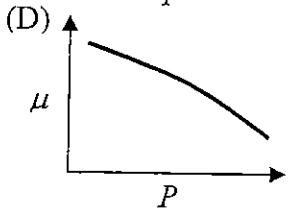
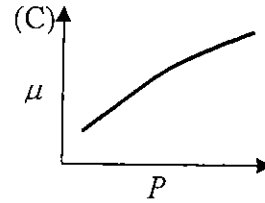
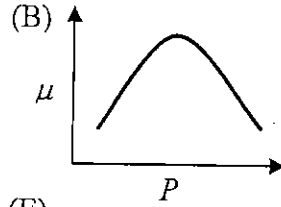
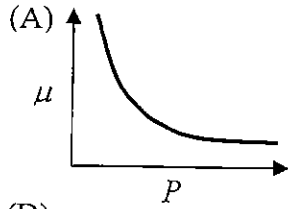


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12. Which of the following figures displays a possible dependence of the chemical potential (μ) on pressure, i.e., $\mu(P)$, of a pure gas?



13. A system of n mole of an ideal gas undergoes an irreversible adiabatic expansion from state 1(P_1, V_1, T_1) to state 2(P_2, V_2, T_2) against a constant external pressure $P_{\text{ex}}=P_2 < P_1$. Which of the following is correct?

(A) $\Delta S = -\frac{P_2(V_2 - V_1)}{T_2 - T_1}$

(B) $\Delta S = C_V \ln \frac{T_2}{T_1}$

(C) $\Delta S = nR \ln \frac{V_2}{V_1}$

(D) $\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$

(E) Because the path is not specified, the entropy change (ΔS) can not be calculated.

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三、問答題(共 50 分)

1. For a quantum system, a particle of mass m is confined to a one-dimensional region $0 \leq x \leq \ell$ with the potential energy

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq \ell \\ \infty & \text{otherwise} \end{cases}$$

- (a) (4分) Write down the energies and normalized wave functions for the stationary state in terms of m , ℓ , and the Planck constant h . What are the allowed values for the quantum number? (You do not need to solve any equation.)
- (b) (4分) Calculate the wavelength of a photon corresponding to a transition between the two lowest energy levels.
2. A particle of mass m moves in one dimension under the influence of a potential energy $V(x)$. Suppose the particle is in an energy eigenstate

$$\psi(x) = \left(\frac{\alpha^2}{\pi}\right)^{1/4} \exp\left(-\frac{\alpha^2}{2}x^2\right)$$

with energy $E = \frac{\hbar^2\alpha^2}{2m}$.

- (a) (3分) Find the mean position of the particle.
- (b) (3分) Find the mean momentum of the particle.
- (c) (6分) What is the potential energy $V(x)$ for the system?
3. A helium atom with mass M moving on the surface of a buckyball can be modeled as a free particle on the surface of a sphere with radius R . Suppose that the state of the atom is described by the normalized wave function

$$\psi(\theta, \phi) = \frac{1}{\sqrt{2}}Y_{1,-1}(\theta, \phi) + \frac{1}{\sqrt{3}}Y_{10}(\theta, \phi) + \frac{i}{\sqrt{6}}Y_{00}(\theta, \phi)$$

where $Y_{\ell m}(\theta, \phi)$ are the spherical harmonics.

- (a) (3分) What is the expectation value of L_z in this state?
- (b) (3分) What is the expectation value of the energy in this state?
4. (a) (4分) Write down the ground-state term symbol for the following atom or ion: (i) H; (ii) F^- .
- (b) (4分) What are the possible values of J for a 2D term? How many states are associated with this term?

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5. Consider an N particle system where at each (distinguishable) site on a lattice there is a *spin* which may point up (high energy) or down (low energy). The energies in the two cases are $E = \Delta > 0$ for spin up and $E = 0$ for spin down. We assume that there are the only two quantum states for the spin at each of the N sites.
- (a) (4分) What is the molecular partition function? What is the canonical partition function for the system? Express these functions in terms of N , Δ , and $\beta (= 1/k_B T)$.
- (b) (4分) What is the numerical value of the molecular partition function as $T \rightarrow 0$, and as $T \rightarrow \infty$?
- (c) (5分) Derive an expression for the average thermal energy $\langle E \rangle$. Evaluate the average thermal energy in the low and high temperature limits ($T \rightarrow 0$ and $T \rightarrow \infty$).
- (d) (3分) Suppose that an experimentalist finds that the population ratio of the system is given by $\frac{n(\text{spin up})}{n(\text{spin down})} = 2$. Use the Boltzmann factor for such population ratio to derive an expression for the effective temperature T which describes this system. Also, what is the sign of this temperature?

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