※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; $\overline{X}$: molar property *X* (example $\overline{S}$: molar entropy)

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

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

(A) For every process in an isolated system, ΔT=0.

(B) For every process in an isolated system, ΔU=0.

(C) For every process in an isolated system, ΔS=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) $dS > đq_{rev}/T$

(B) $dS = đq_{rev}/T$

(C) $dS \geq đq/T$

(D) $dS \leq đq/T$

(E) $\oint \frac{đq}{T} \leq 0$

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

(A) ΔS_X=0

(B) ΔS_X>0

(C) ΔS_{total}=0

(D) ΔS_{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 ξ=0.2 at P=1 bar and T=298.15 K, which of the following is/are correct?

(A) the standard reaction Gibbs energy $\Delta_r G°=0$.

(B) the change of standard Gibbs energy from ξ=0 to ξ=0.2 is zero, i.e., $\Delta G°(\xi=0.2)=0$.

(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 $\Delta_r G°>0$, 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) $\Delta H_{mix}=0$

(B) $\Delta S_{mix}=-2R\ln 2$

(C) $\Delta S_{mix}=2R\ln 2$

(D) $\Delta G_{mix}=-2RT\ln 2$

(E) $\Delta G_{mix}=2RT\ln 2$

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

(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) $\overline{C}_P-\overline{C}_V=R$

(E) $dH=C_P dT$

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

(A) $\left(\frac{\partial \overline{S}}{\partial P}\right)_T=-\frac{R}{\overline{V}-b}$

(B) $\left(\frac{\partial S}{\partial V}\right)_T=\frac{R}{\overline{V}-b}$

(C) $\left(\frac{\partial U}{\partial V}\right)_T=\frac{RT}{\overline{V}-b}$

(D) $\left(\frac{\partial U}{\partial V}\right)_T=0$

(E) $\left(\frac{\partial \overline{H}}{\partial P}\right)_T=b$

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8. Consider a parallel reaction mechanism

$$A \xrightarrow{k_1} B$$

$$A \xrightarrow{k_2} C$$

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

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

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

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, $2O_3 \rightarrow 3O_2$, is believed to proceed through the mechanism

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$O + O_3 \xrightarrow{k_2} 2O_2$$

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

(A) $-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]}{k_{-1}[O_2]}$

(B) $-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_1k_{-1}[O_2] + k_2k_{-1}[O_3]}$

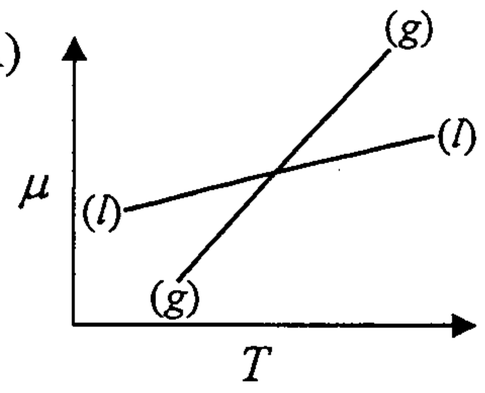
(C) $-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}$

(D) $-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_1k_{-1}[O_2] + k_2k_{-1}[O_3]}$

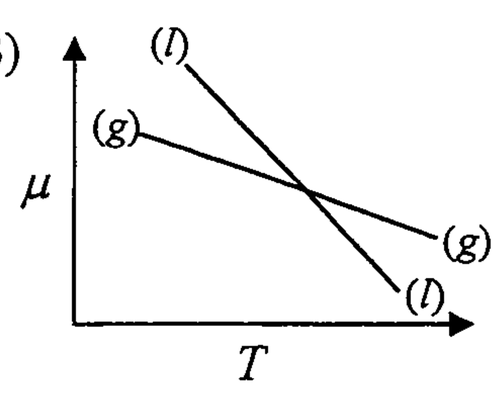
(E) $-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2]}$

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?

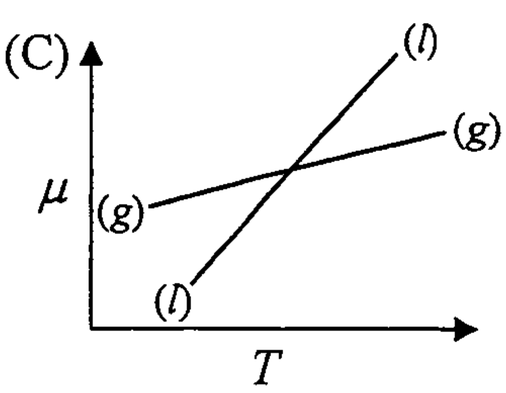
(A)



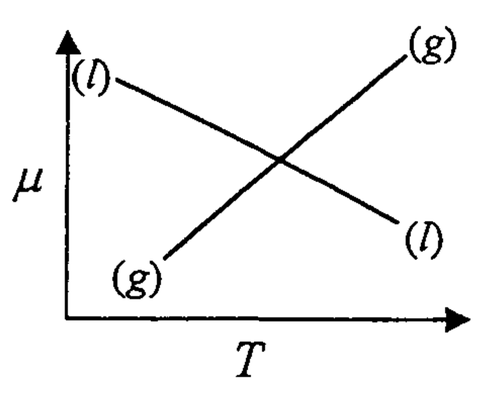
(B)



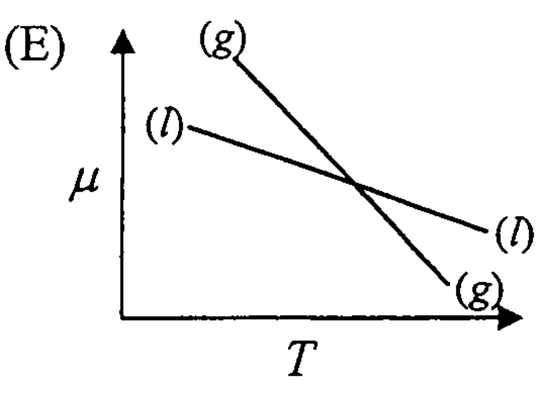
(C)



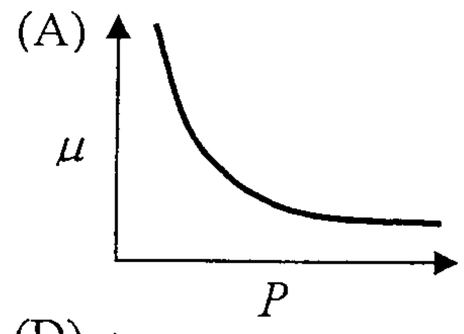
(D)

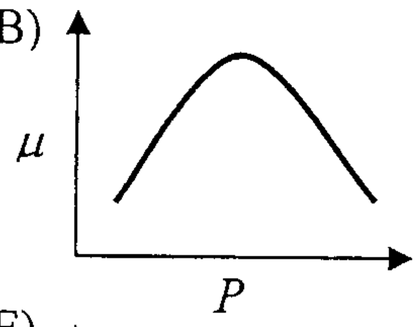


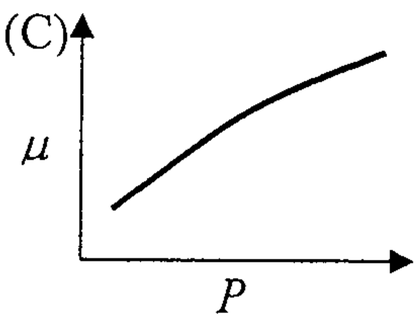
(E)

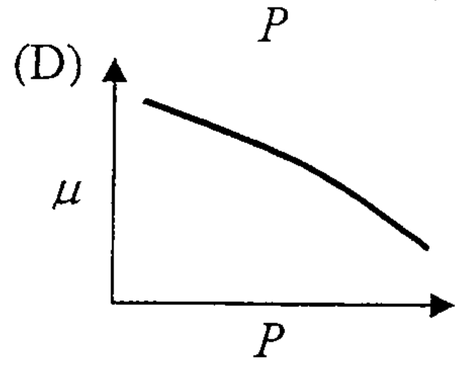


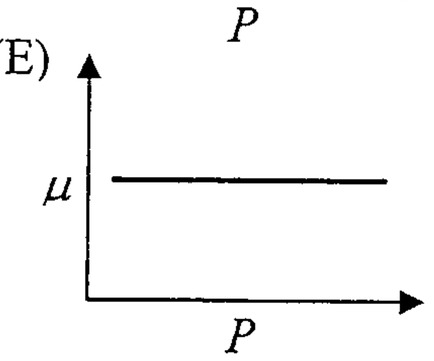
12.Which of the following figures displays a possible dependence of the chemical potential (μ) on pressure, i.e., $\mu(P)$, of a pure gas?

(A)


(B)


(C)


(D)


(E)


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 $P_{ex}=P_2<P_1$. Which of the following is correct?

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

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

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

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

(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 $E = \dfrac{\hbar^2\alpha^2}{2m}$.

(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 $T \to 0$, and as $T \to \infty$?

   (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 ($T \to 0$ and $T \to \infty$).

   (d) (3分) Suppose that an experimentalist finds that the population ratio of the system is given by $\dfrac{n(\text{spin up})}{n(\text{spin down})} = 2$. 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?