第一部分單選題(1-7)，每題 5 分，請務必於試卷第一頁「選擇題作答區」依序作答。

1. Consider a container of total volume V. One mole of ideal gas A at temperature T and volume V_A on one side of the container is separated from one mole of ideal gas B at temperature T and volume V_B on the other side of the container by an impenetrable barrier. Consider that $V=V_A+V_B$. If now we mix the two gases by removing the barrier at constant T and V, what is the total entropy change?

(a) 0 J/K, (b) 0.114 J/K, (c) 5.763 J/K, (d) 11.53 J/K, (e) 13.51 J/K

2. Consider that you have been given a phase diagram for a material for which the following behavior is seen for the coexistence lines: $0 < \left(\frac{dP}{dT}\right)_{sublimation} < \left(\frac{dP}{dT}\right)_{vaporization} < -\left(\frac{dP}{dT}\right)_{fusion}$. If this phase diagram is correct, which of the following properties is unusual?

(a) $\left(\frac{dP}{dT}\right)_{sublimation} > 0$, (b) $\left(\frac{dP}{dT}\right)_{fusion} < 0$, (c) $\left(\frac{dP}{dT}\right)_{vaporization} > 0$, (d) $\left|\left(\frac{dP}{dT}\right)_{fusion}\right| > \left|\left(\frac{dP}{dT}\right)_{sublimation}\right|$,

(e) none of the above

3. Continue from problem 2, which of the following properties violates the second law of thermodynamics, especially near the triple point?

(a) $\left|\left(\frac{dP}{dT}\right)_{fusion}\right| > \left|\left(\frac{dP}{dT}\right)_{sublimation}\right|$, (b) $\left(\frac{dP}{dT}\right)_{vaporization} > \left(\frac{dP}{dT}\right)_{sublimation}$, (c) $\left|\left(\frac{dP}{dT}\right)_{fusion}\right| > \left|\left(\frac{dP}{dT}\right)_{vaporization}\right|$,

(d) $\left(\frac{dP}{dT}\right)_{fusion} < 0$, (e) none of the above

4. The mean solar flux at the Earth's surface is about 2 J/(cm^2 min). Using a non-focusing solar collector, the temperature of the device can reach 85°C. A heat engine is operated using the collector as the hot reservoir and the cold reservoir is at 298 K. What area of the collector is needed to produce 1000 Watts? Assume the engine operates at the maximum Carnot efficiency.

(a) 17.9 m^2, (b) 13.3 m^2, (c) 3.61 m^2, (d) 2.50 m^2, (e) 0.298 m^2

5. Consider two processes involving an ideal gas. In one case, the system undergoes isothermal, reversible expansion from P_1, T_1, V_1 to P_2, T_1, V_2. In the second, the system undergoes reversible, adiabatic expansion from P_1, T_1, V_1 to P_2, T_2, V_2'. Which of the following relationships between properties is correct?

(a) $P_1>P_2$, $T_1>T_2$, $V_2<V_2'$, (b) $P_1<P_2$, $T_1<T_2$, $V_2>V_2'$, (c) $P_1>P_2$, $T_1>T_2$, $V_2>V_2'$, (d) $P_1<P_2$, $T_1>T_2$, $V_2<V_2'$,

(e) $P_1<P_2$, $T_1<T_2$, $V_2<V_2'$

6. The equilibrium constant K_P of the ideal gas reaction, $2NO(g) + O_2(g) \leftrightarrow 2NO_2(g)$, has the value of 2.3×10^{12} at 298 K. Consider that initially there are 2 moles of $NO(g)$ and 1 mole of $O_2(g)$. What is the equilibrium mole fraction of $2NO_2(g)$ expressed in terms of the extent of reaction ξ?

(a) $\frac{2-\xi}{3-\xi}$, (b) $\frac{2-2\xi}{3-\xi}$, (c) $\frac{1-\xi}{3-\xi}$, (d) $\frac{\xi}{3-\xi}$, (e) $\frac{2\xi}{3-\xi}$

7. Continue from problem 6, which of the following approximate expressions for the equilibrium extent of reaction is correct? P is the pressure.

(a) $\xi \approx 1 - \sqrt[3]{\left(\frac{2}{PK_P}\right)}$, (b) $\xi \approx \sqrt{PK_P}$, (c) $\xi \approx 1 - \sqrt{\left(\frac{2}{PK_P}\right)}$, (d) $\xi \approx \sqrt[3]{PK_P}$, (e) none of the above

見背面

第二部分問答或演算題(8-12)，題分註明於問題後方括弧內。

8. For a gas that obeys the Berthelot equation of state, $P = \frac{nRT}{V-nb} - \frac{an^2}{V^2T}$, where P is the pressure, V the volume, T the temperature, R the gas constant, n the number of moles, and a and b are constants, answer the following questions. Show all work and make necessary assumptions.

(a) Derive the expression for the Helmholtz free energy, $A(T,V)$, at constant temperature. **[6 points]**

(b) Derive the expression for the variation of entropy with respect to volume at constant temperature, $\left(\frac{\partial S}{\partial V}\right)_T$. **[4 points]**

(c) Derive the expression for the variation of internal energy with respect to volume at constant temperature, $\left(\frac{\partial U}{\partial V}\right)_T$. **[5 points]**

9. Please explain the difference between pseudo steady state and fast equilibrium approximations. Under what circumstances can you make these assumptions? **[5 points]**

10. Decomposition of a hazardous pollutant in wastewater requires an activation energy of 20 kcal/mol. Assume that a wastewater treatment plant can reduce the concentration of this pollutant to meet the discharge standard using a plug flow reactor (PFR) at 350K. If the cross-sectional area of this PFR is halved, how should the reaction temperature be adjusted to process the same volume of wastewater in the same amount of time? **[15 points]**

11. Suppose that two energy states of a molecule (S_1 and S_2) are involved in a rapid energy transfer equilibrium in N_2 bath:

$$S_2 + N_2 \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} S_1 + N_2$$

Assume that N_2 is in large excess and the initial concentration of S_1 and S_2 are $[S_1]_0$ and $[S_2]_0$, respectively. Derive a mathematical expression for the time development of $[S_1]$. **[15 points]**

12. Assume that the decomposition of ozone in the presence of chlorine follows the mechanism below:

Initiation: $Cl_2 + O_3 \overset{k_1}{\rightarrow} ClO\cdot + ClO_2\cdot$

Propagation: $ClO_2\cdot + O_3 \overset{k_2}{\rightarrow} ClO_3\cdot + O_2$

$$ClO_3\cdot + O_3 \overset{k_3}{\rightarrow} ClO_2\cdot + 2O_2$$

Termination: $2ClO_3\cdot \overset{k_4}{\rightarrow} Cl_2 + 3O_2$

$$2ClO\cdot \overset{k_5}{\rightarrow} Cl_2 + O_2$$

(a) Derive the rate expression for the disappearance of ozone in terms of easily measurable quantities. **[10 points]**

(b) What is the reaction order of $[O_3]$ at long time scale? **[5 points]**

試題隨卷繳回