國立高雄科技大學 113 學年度碩士班招生考試　試題紙

系 所 別：化學工程與材料工程系碩士班　　組　別：乙組

考科代碼：2014　　考　科：物理化學

注意事項：

1、筆試可使用電子計算器之科目，由本校提供，**考生不得使用自備計算器**，違者該科不予計分。

2、請於答案卷上規定之範圍作答，違者該題不予計分。

本試題共 4 題，共 100 分。

Given: R = 0.083145 L bar mol^{-1} K^{-1}

1. Calculate the change in the molar entropy (in $JK^{-1}mol^{-1}$) of isoamyl alcohol when it is vaporized at its boiling point. Isoamyl alcohol boils at 404.4 K at 1.01325 bar, and the molar enthalpy of vaporization is $42822\,J\,mol^{-1}$ at this temperature. If isoamyl alcohol is vaporized into the saturated vapor at this temperature, the process is reversible. Please round numbers in the answer to 2 decimals places. (**15 points**)

2. Work done on the system is considered to the positive. C_P is the heat capacity at constant pressure. C_V is the heat capacity at constant volume. U is internal energy. Proof that

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$ for a closed system and reversible process. (**20 points**)

3. K_P is the equilibrium constant written in terms of pressures. K_c is the equilibrium constant in terms of concentrations. Calculate the value of the equilibrium constant K_c for the dissociation of gas D into gas F, $D(g) \rightleftarrows 2F(g)$ at 600 K. The value of K_P at 600 K is 1.022×10^{-11}. (**15 points**)

4. 單選題(第(1)小題至第(10)小題，每小題 5 分，共 50 分)

(1) m 為氣體分子質量，$\langle v_x^2 \rangle$ 表示氣體分子全體的速率平均值，k_B 稱為波茲曼常數 (Boltzmann constant)，T 為氣體的絕對溫度，則

(A) $m\langle v_x^2 \rangle = k_B T$　(B) $2m\langle v_x^2 \rangle = k_B T$　(C) $m\langle v_x^2 \rangle = 3k_B T$

(D) $4m\langle v_x^2 \rangle = k_B T$

(2) $\mathrm{A} \xrightarrow{k_A} \mathrm{I} \xrightarrow{k_I} \mathrm{P}$，描述連續的一級基本反應，對物質 A 與物質 I 而言，反應速率常數分別為 k_A 與 k_I，反應物 A 會衰減形成中間產物 I，並且這個中間產物會進行連續性反應後形成產物 P。以 $[\mathrm{A}]_0$ 表示物質 A 在 $t=0$ 時的濃度，其餘依此類推。在 $t>0$ 時，以 $[\mathrm{I}]$ 表示物質 I 的濃度，其餘依此類推。$t=0$，僅有反應物 A 存在，即 $[\mathrm{A}]_0 \neq 0$，$[\mathrm{I}]_0 = 0$，$[\mathrm{P}]_0 = 0$，則 $[\mathrm{I}]$ 等於

(A) $\dfrac{k_I}{k_I - k_A}\left(e^{-k_A t} - e^{-k_I t}\right)[\mathrm{A}]_0$　　(B) $\dfrac{k_A}{k_A - k_I}\left(e^{-k_A t} - e^{-k_I t}\right)[\mathrm{A}]_0$

(C) $\dfrac{k_A}{k_I - k_A}\left(e^{-k_A t} - e^{-k_I t}\right)[\mathrm{A}]_0$　　(D) $\dfrac{k_I}{k_A - k_I}\left(e^{-k_A t} - e^{-k_I t}\right)[\mathrm{A}]_0$

(3) 考慮以下正向反應對 A 是一級反應，逆向反應對 B 也是一級反應：

$$\mathrm{A} \underset{k_B}{\overset{k_A}{\rightleftarrows}} \mathrm{B}$$

正向反應和逆向反應的速率常數分別是 k_A 和 k_B。以 $[\mathrm{A}]_0$ 表示物質 A 在 $t=0$ 時的濃度，其餘依此類推。在 $t>0$ 時，以 $[\mathrm{B}]$ 表示物質 B 的濃度，其餘依此類推。$t=0$，僅有反應物 A 存在，即 $[\mathrm{A}]_0 \neq 0$，$[\mathrm{B}]_0 = 0$。在 $t>0$ 時，$[\mathrm{A}]_0 = [\mathrm{A}] + [\mathrm{B}]$，則 $[\mathrm{A}]$ 等於

(A) $[\mathrm{A}]_0 \cdot \left[\dfrac{k_A + k_B e^{-(k_A+k_B)t}}{k_A + k_B}\right]$　　(B) $[\mathrm{A}]_0 \cdot \left[\dfrac{k_A + k_B e^{-(k_A+k_B)t}}{k_A - k_B}\right]$

(C) $[\mathrm{A}]_0 \cdot \left[\dfrac{k_B + k_A e^{-(k_A+k_B)t}}{k_A - k_B}\right]$　　(D) $[\mathrm{A}]_0 \cdot \left[\dfrac{k_B + k_A e^{-(k_A+k_B)t}}{k_A + k_B}\right]$

(4) d_N 為氣體分子數量密度，P 為氣體壓力，k_B 為波茲曼常數(Boltzmann constant)，T 為氣體的絕對溫度，則 d_N 等於

(A) $\dfrac{P^4}{k_B^4 T^3}$　　(B) $\dfrac{P^3}{k_B^3 T^2}$　　(C) $\dfrac{P^2}{k_B^2 T}$　　(D) $\dfrac{P}{k_B T}$

(5) Joule-Thomson 膨脹實驗屬於

(A) 恒內能程序　　(B) 恒焓程序　　(C) 恒熵程序　　(D) 恒自由能程序

(6) N_A is Avogadro constant. R is the gas constant. Ω is the number of equally probable microscopic arrangements for the system. S is entropy. S is equal to

(A) $(N_A)\cdot(e^{\Omega})$ (B) $(\Omega)\cdot(\ln N_A)$ (C) $[(R)\cdot(\ln\Omega)]\div(N_A)$

(D) $(\ln\Omega)\div[(R)\cdot(N_A)]$

(7) The maximum partial pressure of water vapor in air at equilibrium at a given temperature is the vapor pressure of water at that temperature. The actual partial pressure of water vapor in air is a percentage of the maximum, and the percentage is called the relative humidity. Suppose the relative humidity of air is 40% at a temperature of 25°C. The vapor pressure of water at 25°C is 3186 Pa. Assume that the gas mixture behaves as an ideal gas. If the atmospheric pressure is 1.2 bar, what is the mole fraction of water in the air?

(A) 0.01062 (B) 0.01593 (C) 0.0229 (D) 0.0345

(8) T represents temperature. q represents heat. S represents entropy. $\oint\frac{dq}{T}>0$ occurs in

(A) an impossible process (B) a reversible process (C) an irreversible process

(9) Work done on the system is considered to the positive. S represents entropy. U represents internal energy. V represents volume. P represents pressure. T represents temperature.

$\left(\frac{\partial S}{\partial V}\right)_T$ equals

(A) $\frac{1}{T}\left[P-\left(\frac{\partial U}{\partial V}\right)_T\right]$ (B) $-T\left[P+\left(\frac{\partial U}{\partial V}\right)_T\right]$ (C) $\frac{1}{T}\left[P+\left(\frac{\partial U}{\partial V}\right)_T\right]$

(D) $T\left[P-\left(\frac{\partial U}{\partial V}\right)_T\right]$

(10) Work done on the system is considered to the positive. S represents entropy. H represents enthalpy. V represents volume. P represents pressure. T represents temperature.

$\left(\frac{\partial S}{\partial P}\right)_T$ equals

(A) $\frac{1}{T}\left[V+\left(\frac{\partial H}{\partial P}\right)_T\right]$ (B) $-T\left[\left(\frac{\partial H}{\partial P}\right)_T-V\right]$ (C) $-\frac{1}{T}\left[V+\left(\frac{\partial H}{\partial P}\right)_T\right]$

(D) $T\left[\left(\frac{\partial H}{\partial P}\right)_T-V\right]$