系所組別： 化學系
考試科目： 物理化學
考試日期：0223，節次：1

※ 考生請注意：本試題不可使用計算機。 請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

$\ln 2=0.7$ $\ln 3=1.1$ $\ln 10=2.3$ $R=8.3\ J\ K^{-1}\ mol^{-1}=0.08\ L\ atm\ K^{-1}\ mol^{-1}$

(1) (a) Write down the third law of thermodynamics.
(b) According to the Boltzmann formula for entropy, write down the entropy (in $J\ K^{-1}$) for the following state: a nearly perfect, atomic crystal containing 6×10^{23} atoms at 0 K with one atom not at its lattice site. (6 分)

(2) Write down the entropy change (in $J\ K^{-1}$) when argon at 27 °C and 1.0 atm in a container of volume 0.5 dm^3 is allowed to expand to 1.0 dm^3 and is simultaneously heated to 327 °C. (10 分)

(3) For the orbital energy of H atom, $E_n=-2.2\times10^{-18}/n^2$ (J). Write down the (a) energy of 3d orbital, (b) orbital angular momentum of a 3d electron, (c) components of the angular momentum in the direction of an external magnetic field (z axis), (d) magnetic moments on the z axis, and (e) ionization energy of a H atom at ground state. (f) Describe the state as the electron is at $n=\infty$, i.e. E=0. (14 分)

(4) For the particle in an one-dimensional box with the boundaries at x=0 and L, $\psi(x)=(2/L)^{1/2}\sin(n\pi x/L)$. Write down the positions of nodes inside the box with the particle at n=5. (5 分)

(5) $Cu^{2+} + 2e^- \rightarrow Cu$ $\varepsilon^o=0.34$ V, $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $\varepsilon^o=0.77$ V
(a) Write down the galvanic cell potential (ε^o_{cell}) (b) Write down the cell potential as $[Fe^{2+}]=1.0$ M, $[Fe^{3+}]=0.1$ M, $[Cu^{2+}]=10.0$ M at 25 °C. (6 分)

(6) For $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$ (27 °C)
It is known that $\Delta G=-21846\ J\ mol^{-1}$ at $[H_2]=1.0$ atm, $[N_2]=1.0$ atm, and $[NH_3]=10.0$ atm. Write down the equilibrium constant (K). (6 分)

(背面仍有題目, 請繼續作答)

編號： 46

國立成功大學103學年度碩士班招生考試試題

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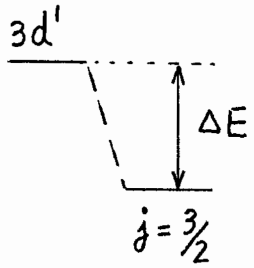
(7) For a linear rotor, given that the energy difference between J=3 and J=5 is 54 cm^{-1}, write down the energy difference (in cm^{-1}) between J=2 and J=4. (6 分)

(8) Spin-orbit coupling constant = 12 cm^{-1}. Write down ΔE in cm^{-1}. (6 分)



(9) The reaction $2AB + C_2 \rightarrow A_2B + C_2B$ has the mechanism of

$$2\,AB \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_2B_2 \qquad A_2B_2 + C_2 \xrightarrow{k_2} A_2B + C_2B$$

Calculate the differential rate law (hint: using steady state approximation. Show your calculation procedure). (6 分)

(10) Draw potential energy curves to explain (a) fluorescence and (b)Franck-Condon principle. (10 分)

(11) (a)What is the gross selection rule of pure rotational spectra (b) Explain the Stark effect. (10 分)

(12) In absorption vibration-rotation spectra of polyatomic molecules, there may exist P, Q and R bands. Explain these bands. But for Raman vibration-rotation spectra, there may have O, Q, and S branches. Explain them. (10 分)

(13) Prove that the Joule-Thomson effect is a process without change of entropy. (5 分)