

科目：物理化學 適用：應化所

編號：444

考生注意：

1. 依次序作答，只要標明題號，不必抄題。
2. 答案必須寫在答案卷上，否則不予計分。
3. 限用藍、黑色筆作答；試題須隨卷繳回。

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1. Please prove that

$$(a) \left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P \quad (8\%)$$

$$(b) C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P \quad (8\%)$$

$$(c) \left( \frac{\partial S}{\partial T} \right)_P = C_P / T \quad (8\%)$$

2. The reaction,  $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$ , relaxes to equilibrium with a relaxation time of  $25.0 \mu\text{s}$  at  $298 \text{ K}$  and  $\text{pH} = 7.0$  and  $\text{pKw} = 14.0$ . Given that the forward reaction is first order and the reverse is second-order overall and the molar concentration of pure water is  $50 \text{ mol L}^{-1}$ . Please calculate the rate-constant for the (a) forward reaction (8%) and (b) reverse reaction. (8%)

3. For a particle in one dimensional well of infinite depth with the length

$$L. \text{ The normalized wave function is } \psi_n(x) = \left( \frac{2}{L} \right)^{\frac{1}{2}} \sin \left( \frac{n\pi x}{L} \right).$$

- (a) Please determine the expectation values  $\langle X \rangle$  and  $\langle X^2 \rangle$  of the particle. (10%)

- (b) Please determine the expectation values  $\langle P_x \rangle$  and  $\langle P_x^2 \rangle$  of the particle. (10%)

- (c) Please justify the uncertainty of the position and its conjugated momentum in the above case with  $n=1$ , that  $\sigma_X \sigma_{P_x} \geq h/4\pi$ . Where  $\sigma_X$  is the standard deviation of the observable  $X$  and  $h$  is the plank constant. (10%)

$$h = 6.626 \times 10^{-34} \text{ Js.}$$

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4. For a two-level system, the lower energy state is non-degenerated and the higher energy state (at an energy  $\varepsilon$ ) is doubly degenerated.
- (a) Please write down the partition function  $q$  for the system. (5%)
- (b) Please calculate the population at  $T \rightarrow 0$ . (5%)
- (c) Please calculate the population at  $T \rightarrow \infty$ . (5%)
5. A cell in which the reaction,  $\text{Pb} + \text{Hg}_2\text{Cl}_2 \rightarrow \text{PbCl}_2 + 2\text{Hg}$ , takes place has an electromotive force (emf) of 0.5 V at 300 K, and this emf increases with temperature by  $1.5 \times 10^{-4}$  V/K.
- (a) Please calculate the maximum available work per mole of Pb dissolved from the cell at 300 K. (5%)
- (b) Please calculate the entropy of the reaction at 300 K. (5%)
- (c) Please calculate the heat absorbed by the cell at 300 K per mol of Pb dissolved. (5%)