

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

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

(c) $\left(\frac{\partial S}{\partial T}\right)_P = C_p / T$ (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 K and $\text{pH} = 7.0$ and $\text{pK}_w = 14.0$. Given that the forward reaction is first order and the reverse is second-order overall and the molar concentration of pure water is 50 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. The normalized wave function is $\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)$.

(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 σ_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 ϵ) 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 1.5×10^{-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%)

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