元智大學 102 學年度研究所 **碩士班** 招生試題卷

系(所)別：化學工程與材料 科學學系碩士班　組別：不分組-選考B　科目：物理化學　用紙第 / 頁共 / 頁

●可使用現行『國家考試電子計算器規格標準』規定第二類之計算機

I. Mark "Truth" or "False" for the following statements, and explain why? (40%; 4% each)

(1) The entropy change for a perfect gas expanding isothermally and reversibly from V_i to V_f, is the same for the gas expanding isothermally and freely between the same two volume.

(2) The equilibrium constant of an exothermic reaction decreases with an increase in temperature.

(3) The reaction rate varies steeply with temperature for the reaction having higher activation energy.

(4) The chemical potential of the liquid solvent increases as a result of the presence of a solute.

(5) For constant quantity of macromolecule dissolved in solvent, the higher the molar masses the lower osmotic pressure it produces.

(6) The Gibbs energy of reaction: $CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g)$, decreases with increasing temperature.

(7) For the Daniel cell $Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$, the cell potential increases with increasing concentration of $CuSO_4(aq)$.

(8) At low concentrations of added NaBr(s), the solubility of the AgCl(s) is increased.

(9) The half-life of a first-order reaction lengthens as the concentration of reactant falls.

(10) The pK_a of the weak acid is equal to the pH half-way to the stoichiometric point of the titration of a weak acid with a strong base.

II. For the Langmuir isotherm, the free gas and the monolayer adsorbed gas are in dynamic equilibrium: $A_{(g)} + M_{(surface)} \leftrightarrows AM_{(surface)}$ with rate constant k_a for adsorption and k_d for desorption. Derive the Langmuir isotherm $\theta = \frac{Kp}{1+Kp}$ for the variation of the fractional coverage θ with pressure at a chosen temperature where θ depends on the pressure p of the overlying gas and the equilibrium constant K equals to k_a/k_d. At constant temperature, various adsorbed gas volume V according to different pressures p fits the Langmuir isotherm. How to obtain V_∞ the volume corresponding to complete coverage and the equilibrium constant K? (15%)

III. Derive the Clapeyron equation: $\frac{dP}{dT} = \frac{\Delta_{vap}S}{\Delta_{vap}V}$ for the liquid–vapour boundary and estimate the typical size of the effect of increasing pressure by 0.1 atm on the boiling point of a liquid. (15 %) (*Hint*: using the Trouton's rule and the perfect gas law; where P denotes pressure, T temperature, $\Delta_{vap}S$ and$\Delta_{vap}V$ for entropy change and volume change during vaporization, respectively)

IV. The reaction A + B → P is first-order in each of two reactants A and B. Show that the rate law: $v = k[A][B]$ and $kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[B]/[B]_0}{[A]/[A]_0}$, where $[A]_0$ and $[B]_0$ denote the initial concentration of reactants A and B, respectively. (15 %)

V. An ideal gas expands from initial volume V_i to final volume V_f. Calculate the changes ΔU, Q and W for the gas (in terms of n, T, V_i and V_f) under the following process: (1) free expansion into vacuum; (2) adiabatic expansion starts at temperature T_0; (3) isothermal expansion starts at temperature T_0. (15%; 5% each)