國立成功大學 76 學年度研究所入學考試（ 物理化學 試題） 共 2 頁 第 1 頁

1. Given the Maxwell distribution function of molecular speeds $f(v) = (m/2\pi kT)^{\frac{3}{2}} 4\pi v^2 \exp(-mv^2/2kT)$, derive the most probable speed v_{mp}. (5%)
2. Derive the expression for the half-life of a reaction with the rate law: $-\frac{d[A]}{dt} = k[A]^{\frac{1}{2}}$. (5%)
3. Calculate the temperature at which 10% of the molecules in a system will be in the first excited electronic state which is 400 KJ/mol above the ground state. (5%)
4. If identical hard spheres are packed according to a body-centered cubic lattice, Calculate the fraction of volume occupied by spheres. (5%)
5. At 25°c the conductivity κ of the pure water is $5.5\times10^{-6}\ \Omega^{-1}m^{-1}$. The limiting ion mobilities of H^+ and OH^- ions are 36.25×10^{-8} and 20.64×10^{-8} $m^2V^{-1}s^{-1}$, respectively. Calculate the ion product constant K_w for water. (6%)
6. The rate law for $2NO_2 \rightarrow 2NO + O_2$ reaction is $-\frac{d[NO_2]}{dt} = k[NO_2]^2$ with $k = 6.3\times10^2$ mL/mol·s at 600K. How long will it take for 10% of NO_2 (at 400mmHg initially) to decompose by this reaction? (8%)
7. (a) Show that the dissociation pressure (p) of ammonium carbamate:
   $NH_2COONH_2(s) \rightleftarrows 2NH_3(g) + CO_2(g)$
   is related to the equilibrium constant as $K_p = \frac{4}{27}P^3$. (4%)
   (b) At 25°C, the total pressure of the above reation is 0.117atm. Calculate ΔG°_f of ammonium carbamate. (4%)
   Given: $\Delta\bar{G}^\circ_{f.NH_3(g)} = -16.45\ KJ\ mol^{-1}$, $\Delta\bar{G}^\circ_{f.CO_2(g)} = -394.36\ KJ\ mol^{-1}$.
8. Assume that benzene and toluene form ideal solutions, pure benzene boil at 80°c; at that temperature toluene has a vapor pressure of 350 torr.
   (a) Calculate the partial and total pressure of a solution at 80°c. with mole fraction of benzene is 0.2? (4%)
   (b) What composition of solution would boil at 80°C under a reduced pressure of 500 torr? (4%)
9. An ideal monoatomic gas expands adiabatically from 800K, 8 atm to 1atm final pressure. Calculate ΔS, ΔU and q for the process if it is (a) reversible (b) irreversible, doing 3000J of work, (c) irreversible against zero pressure. (9%)

（背面還有題目）

10. For the cell $Pb(s) | Pb^{2+}(0.0125M) \| Ag^{+}(0.600M) | Ag(s)$, Calculate E°_{cell} and E_{cell}. Write the net cell reaction and Calculate K_{eq}. Predict the spontaneous direction of reaction from the sign of E_{cell}. (9%)

$Ag^{+} + e^{-} \rightarrow Ag(s)$ $\quad E^{\circ} = 0.799$ volts

$Pb^{2+} + 2e^{-} \rightarrow Pb(s)$ $\quad E^{\circ} = -0.126$ volts

11. A particle is moving in one dimension between $x = a$ and $x = b$. The potential energy is such that the particle cannot be outside these limits and that the wavefunction is $\psi = \frac{A}{x}$.

(a) determine the normalization constant A. (5%)

(b) Calculate the expectation value of x. (5%)

12. For the following molecules: $CHCl_3$, C_3H_6 (cyclopropane), CO_2 (linear),

(a) give the symmetry elements and the point group. (6%)

(b) which one has dipole moment? (2%)

(c) which one has pure rotational spectra? (2%)

13. Write: (a) the hybrid orbitals,
(b) the number of lone pairs in the central atom,
and (c) the shapes of the following molecules or ions.

$BeCl_2$, NH_3^{2+}

(atomic number: $Be = 4$ $\quad N = 7$)