國立臺灣科技大學
九十三學年度碩士班考試試題

系所組別：高分子工程系丁組
科　　目：物理化學

總分100分

1. (8%) A solution of the sugar mannitol (mol wt 182.2) is prepared by adding 54.66g of mannitol to 1000 g of water. The vapor pressure of pure liquid water is 17.54 torr at 20°C. Mannitol is nonvolatile and does not ionize in aqueous solutions.
   (a) Assuming that aqueous mannitol solutions behave ideally, calculate the vapor-pressure lowering (the difference between the vapor pressure of pure water and that of the solution) for the above solution at 20°C.
   (b) The observed vapor-pressure lowering of the mannitol solution above is 0.0930 torr. Calculate the activity coefficient (based on mole fraction) of water in this solution.

2. (7%) A reaction is zero order in substance S. Starting with the differential rate law, derive an expression for $t_{1/2}$ in terms of the starting concentration $[S]_0$ and the zero-order rate constant k. $t_{1/2}$ = half-life

Values of Physical Constants

Quantity	*Symbol*	*Value*[a,b]	*Units*
Acceleration due to gravity	g	9.806 65(exact)	$m\ s^{-2}$
Speed of light in vacuum	c	299 792 458 (exact)	$m\ s^{-1}$
Permeability of vacuum	μ_0	$4\pi \times 10^{-7}$ (exact)	$N\ A^{-2}$
		= 12.566 370 614...	$10^{-7}\ N\ A^{-2}$
Permittivity of vacuum	ε_0	$1/\mu_0 c^2$ (exact)	$C^2\ N^{-1}\ m^{-2}$
		= 8.854 187 817...	$10^{-12}\ C^2\ N^{-1}\ m^{-1}$
Planck constant	h	6.626 075 5(40)	10^{-34} J s
$h/2\pi$	$\hbar$	1.054 572 66(63)	10^{-34} J s
Elementary charge	e	1.602 177 33(49)	10^{-19} C
Bohr magneton, $e\hbar/2m_e$	μ_B	9.274 015 4(31)	$10^{-24}\ J\ T^{-1}$
Nuclear magneton, $e\hbar/2m_p$	μ_N	5.050 786 6(17)	$10^{-27}\ J\ T^{-1}$
Rydberg constant, $m_e e^4/8h^3 c\varepsilon_0$	R_∞	10 973 731.534(13)	m^{-1}
Bohr radius, $h^2\varepsilon_0/\pi m_e e^2$	a_0	0.529 177 249(24)	10^{-10} m
Hartree energy, $e^2/4\pi\varepsilon_0 a_0$	E_h	4.359 748 2(26)	10^{-18} J
Electron mass	m_e	9.109 389 7(54)	10^{-31} kg
Proton mass	m_p	1.672 623 1(10)	10^{-27} kg
Neutron mass	m_n	1.674 928 6(10)	10^{-27} kg
Deuteron mass	m_d	3.343 586 0(20)	10^{-27} kg
Avogadro constant	N_A	6.022 136 7(36)	$10^{23}\ mol^{-1}$
Atomic mass constant, $m_u = (1/12)m(^{12}C)$	m_u	1.660 540 2(10)	10^{-27} kg
Faraday constant	F	96 485.309(29)	$C\ mol^{-1}$
Gas constant	R	8.314 510(70)	$J\ K^{-1}\ mol^{-1}$
		0.083 145 1	$L\ bar\ K^{-1}\ mol^{-1}$
		1.987 216	$cal\ K^{-1}\ mol^{-1}$
		0.082 057 8	$L\ atm\ K^{-1}\ mol^{-1}$
Boltzmann constant, R/N_A	k	1.380 658(12)	$10^{-23}\ J\ K^{-1}$

[a] E. R. Cohen and B. N. Taylor, The 1986 CODATA Recommended Values of the Fundamental Physical Constants. *J. Phys. Chem. Ref. Data* 17:1795 (1988).
[b] Digits in parentheses are the one-standard-deviation uncertainty in the last digits of the given value.
[c] More recent values of physical constants are available on the web site of the National Institute of Standards and Technology (http://physics.nist.gov/constants).

3. (8%) The fundamental vibration frequency of gaseous $^{14}N^{16}O$ is1904 cm^{-1}.
   (a) Calculate the fundamental vibration frequency of gaseous $^{15}N^{16}O$.
   (b) Sketch an energy-level diagram for this problem.
   Use $E_v = \left(v + \frac{1}{2}\right)h\nu_0$ $\qquad \nu_0 = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$

4. (7%) For the 1s orbital of the hydrogen atom, calculate the probability of finding the electron within a distance a_0 (the Bohr radius) from the nucleus.

TABLE Hydrogenic Wavefunctions

$$\psi(1s) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$\psi(2s) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$\psi(2p_z) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2}(z)\, e^{-Zr/2a_0}$$

$$\begin{cases} \psi(2p_x) = \dfrac{1}{4\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{5/2}(x)\, e^{-Zr/2a_0} \\ \psi(2p_y) = \dfrac{1}{4\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{5/2}(y)\, e^{-Zr/2a_0} \end{cases}$$

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5. (6%) Predict the rate law for the reaction

$2O_3 \leftrightarrow 3O_2$

from the following mechanism

1. $O_3 \leftrightarrow O_2 + O$
2. $O + O_3 \rightarrow 2O_2$

6. (10%) **The first order rate constant, k_1, for the thermal decomposition of nitrogen pentoxide increases with temperature as shown below**

$k_1/10^{-5}s^{-1}$	3.4	13.5	76	487
Temperature/K	298	308	323	338

Evaluate the activation energy, E_a, and the Arrhenius pre-exponential factor, A, for this reaction.

7. (10%) 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 the wave function in between is Ψ = A/x, (a) Determine the normalization constant; (b) Calculate the average value of x.

8. (6%) Write the Hamiltonian of (a) free-rigid rotor; (b) H_2.

9. (8%) Absorption by $H^{35}Cl$ occurs in the far infrared near 200 cm^{-1}, and the spacing between the neighboring lines is 20.89 cm^{-1}. Find the moment of inertia and the internuclear distance in $H^{35}Cl$.

10. (15%) P and N are of the same group. Their configurations are similar.
(a) What is the orbital configuration of P_2?
(b) What is the bond order?
(c) What is the paramagnetism?

11. (15%) The diffusivity of hemoglobin in water is 6.9×10^{-7} cm^2/s at 20°C.
(a) Estimate its molecular diameter.
(b) Calculate the viscosity of water at 37°C.
(The viscous activation energy of water is 12.1 kJ/mol, and the viscosity of water at 20°C is 1 mPa-s.)
(c) What is the diffusivity of hemoglobin at human body temperature (37°C)?