科目：物理化學(2004)　　校系所組：中大化學學系　交大應用化學系甲組　清大化學系

R= 8.314 J/(K mole)

1. For dry air at 1.0000 atm pressure, the densities at –50°C, 0°C, and 69°C are 1.5826 g dm^{-3}, 1.2929 g dm^{-3}, and 1.0322 g dm^{-3}, respectively. From these data, and assuming that air obeys Charles's law, determine a value for the absolute zero of temperature in degrees Celsius. **(10%)**

2. Consider a system consisting of 3.0 mol $CO_2(g)$, initially at 35°C and 9.0 atm and confined to a cylinder of cross-section 100.0 cm^2. The sample is allowed to expand adiabatically against an external pressure of 2.5 atm until the piston has moved outwards through 25 cm. Assume that carbon dioxide may be considered a perfect gas with $C_{V,m}$ = 28.8 J K^{-1} mol^{-1}, and calculate (a) q, (b) w, (c) ΔU, (d) ΔT, (e) ΔS. **(20%)**

3. The equilibrium constant of a reaction is found to fit the expression $\ln K = A + B/T + C/T^2$ between 400 K and 600 K with $A = -1.76$, $B = -1368$ K, and $C = 1.1 \times 10^5$ K^2. Calculate the standard reaction enthalpy and standard reaction entropy at 500 K. **(20%)**

4. (a) If A is an operator, then the exponential operator e^A is defined as a power series: $e^A = \sum_n (\frac{1}{n!})A^n$. If the eigenfunction f(x) of the operator A with an eigenvalue a, what is the eigenvalue of e^A when the exponential operator e^A operates on f(x). Show your answer? **(2%)**

(b) Define an operator function $f(\lambda) = e^{A\lambda}Be^{-A\lambda}$, where A and B are two operators and λ is a parameter. Show that (i) f(0) = B, (ii) $\frac{df(\lambda)}{d\lambda} = [A, f(\lambda)]$ and (iii) $\frac{d^2 f(\lambda)}{d\lambda^2} = [A,[A, f(\lambda)]]$. **(5%)**

(c) By setting λ = 1, then the operator function $f(\lambda) = e^{A\lambda}Be^{-A\lambda}$ can be shown as $e^A Be^{-A} = B + [A,B] + \frac{1}{2!}[A,[A,B]] + \frac{1}{3!}[A,[A,[A,B]]] + ...$ When a sandwich operator R_A is defined as $R_A = e^{-iHt} A e^{iHt}$, where both A and H are operators, i = $\sqrt{-1}$, and t represents time, then answer the following questions:

(i) Simplify the expression $e^{-i\omega Lzt} L_z e^{i\omega Lzt}$, where L_z is the z-component of the angular momentum operator and ω is a constant? **(2%)**

(ii) Simplify the function $e^{-i\omega Lzt} L_y e^{i\omega Lzt}$ as a combination of cosine and sine functions, where L_y is the y-component of the angular momentum operator. **(4%)**

注意：背面有試題

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5. Single-walled carbon nanotubes can be approximated by a particle-on-a-cylindrical-surface model. Suppose the cylinder has length L and radius a, with the z-axis along the cylinder.

(a) Write the kinetic energy Hamiltonian of the electron in terms of the length z, the radius a, and the radial angle ϕ of the cylinder. **(4%)**

(b) Combining ideas from the particle-in-a-box and 2-D rigid-rotor models, show that the wavefunction can be written as $\psi = A\sin(n\pi z/L)e^{im\phi}$, where A is a constant. What are the allowed values of the quantum numbers n and m? **(6%)**

(c) Write the energy expression in terms of m, n, L, a, and fundamental constants. **(4%)**

6. It is convenient to write the integrals that appear in quantum mechanics using the following *Dirac notation*: $\int \phi^* A \psi d\tau = <\phi|A|\psi>$. The $<\phi|$ that appears in this formula is termed a "bra", and the $|\psi>$ is called a "ket". Note that the complex conjugation operation is assumed in writing the bra. If $|\alpha>$ and $|\beta>$ are two basis sets of a spin system, then these spin states can be expressed as matrices as follows:

$$|\alpha> = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\beta> = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, <\alpha| = \begin{pmatrix} 1 & 0 \end{pmatrix}, \text{ and } <\beta| = \begin{pmatrix} 0 & 1 \end{pmatrix}.$$

The wavefunction of the system can be given by $|\psi> = a|\alpha> + b|\beta>$, where a and b are two coefficients. Please answer the following questions:

(a) What are the expressions of (a) $<\alpha|\alpha>$, (b) $<\beta|\alpha>$, (c) $<\psi|$, (d) $<\alpha|\psi>$, (e) $<\psi|\psi>$, and (f) $|\psi><\psi|$ in terms of a and b whenever possible? **(12%)**

(b) What is the value of $\sum_{s=\alpha,\beta} |s><s|$ **(3%)**

7. The Fermi contact interaction is a coupling between the nuclear and electron spins and its Hamiltonian has the form:

$$H(\text{Fermi}) = A\mathbf{s}\bullet\mathbf{I}$$

where A is a constant and **s** and **I** are the spin operators for the electrons and nucleus, respectively. Consider a hydrogen atom in its ground state.

(a) What is the expectation value of H(Fermi) for the four possible combinations of electronic and nuclear spin states (i.e., $m_s = \pm\frac{1}{2}$ and $m_N = \pm\frac{1}{2}$)? **(4%)**

(b) If the constant A in this case is 9.46571×10^{-25} joule, what resonance wavelength is associated with EPR transitions (wherein the electron spin changes quantum numbers while the nuclear spin is unchanged)? **(4%)**

(note: Planck constant $h = 6.626 \times 10^{-34}$ joule•s and speed of light $c = 3 \times 10^8$ m/s)