科目：物理化學(2004) 校系所組：中央大學化學學系 交通大學應用化學系 清華大學化學系

1. Consider a cell of length b containing an absorbing substance with concentration c and a beam of light with a wavelength λ passing through it. The intensities of the incident light and the transmitted light are $I_0(\lambda)$ and $I(\lambda)$, respectively. Derive that the absorbance $A(\lambda)$ is linear to b and c under dilute condition,

$$A(\lambda)=\log_{10}\left(\frac{I_0(\lambda)}{I(\lambda)}\right)=a(\lambda)\cdot b\cdot c$$

where $a(\lambda)$ is the extinction coefficient. (10%)

2. A rotational-vibrational absorption spectrum for HCl was measured at a temperature T. Assume that the harmonic oscillator-rigid rotor approximation applies. The vibrational energy is $h\nu_e(v+1/2)$, where v is the vibrational quantum number. The rotational energy is $hcB_eJ(J+1)$ and the energy level is (2J+1)-fold degenerate, where J is the rotational quantum number. For HCl, ν_e= 2990.9 cm^{-1} and B_e= 10.593 cm^{-1}. The Boltzmann distribution is given

$$\text{population of level i} \propto g_i\cdot\exp\left(\frac{E_i}{k_BT}\right)$$

where g_i and E_i are the degeneracy and the level energy of level i, respectively.

(a) The most intense spectral lines in the spectrum were found to correspond to transitions from J=3. Estimate the temperature T. (8%)

(b) Find the wavelength (in nm) of the first line in the P branch (ΔJ = -1) of the first overtone vibrational band. (8%)

(h= 6.626x10^{-34} J s; , c= 2.99x10^{8} m s^{-1}; k_B= 1.3807x10^{-23} J K^{-1})

3. In the discussion of the Lindemann mechanism for unimolecular reactions, the reactant molecule *A* can be activated by collision with another *A* or by collision with a nonreactant molecule *M*. If the rates of activation for these two processes are different, the mechanism becomes

$$A+M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^*+M$$

$$A+A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A^*+A$$

$$A^* \xrightarrow{k_3} P$$

What is the rate law expression for this mechanism (d[P]/dt=?)? (14%)

4. If a dilute monatomic gas with a mass of *m* is in a box with a volume of *V*, the internal energy *U* and the translational partition function (q_{tr}) can be expressed as

$$U=-N\left(\frac{\partial \ln q}{\partial\beta}\right)_V=Nk_BT^2\left(\frac{\partial q}{\partial T}\right)_V \quad \text{where } \beta=\frac{1}{k_BT}\ ; \qquad q_{tr}=\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}V$$

Now consider an ideal monatomic gas confined to move on a surface.

(a) What is the contribution to the internal energy from translations? (6%)

(b) What is the expected contribution from the equipartition theorem? (4%)

注意：背面有試題

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5. The wavefunction of an electron in a one-dimensional infinite square well of width a, $x \in (0,a)$, at time $t=0$ is given by $\Psi(x,0)=\sqrt{3/7}\psi_1(x)+\sqrt{4/7}\psi_2(x)$, where $\psi_1(x)$ and $\psi_2(x)$ are the ground state and the first excited stationary state of the system for $t=0$. ($\psi_n(x)=N\sin(n\pi x/a)$, $E_n=n^2\pi^2\hbar^2/(2ma^2)$)
   (a) Write down the wavefunction $\Psi(x,t)$ at time t in terms of $\psi_1(x)$ and $\psi_2(x)$. (5%)
   (b) Calculate the normalization constant N. (5%)
   (c) Calculate the expectation value of the energy $\langle E\rangle$ in the state $\Psi(x,t)$ above. (5%)
   (d) Write down the stationary states for $n=1,2$ explicitly. (5%)

6. (a) Two vessels contain two identical ideal gases at the same temperature T and with equal numbers of particles N but at different pressures P_1 and P_2. The vessels are then connected. Find the change in entropy. (10%)
   (b) Two identical ideal gases at the same pressure P and containing the same number of particles N but at different temperatures T_1 and T_2 are in vessels with volumes V_1 and V_2. The vessels are then connected. Find the change in entropy. (10%)

7. A thermal system is constrained to constant mole number and volume, so that no work can be done on or by the system. The heat capacity of the system is C, constant. The fundamental equation of the system, for constant volume, is $S=S_0+C\ln(U/U_0)$, so $U=CT$. S and U are entropy and energy, respectively. Consider a thermodynamic system that consists of two such thermal systems. The two systems, with equal heat capacities, have initial temperatures T_1 and T_2, with $T_1<T_2$. What is the maximum total work that can be delivered from the two thermal systems? (10%)