

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 $hcB_e J(J+1)$ and the energy level is $(2J+1)$ -fold degenerate, where J is the rotational quantum number. For HCl, $\nu_e = 2990.9 \text{ cm}^{-1}$ and $B_e = 10.593 \text{ cm}^{-1}$. The Boltzmann distribution is given

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

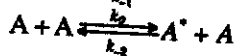
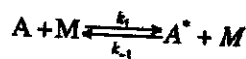
where g_i and E_i are the degeneracy and the level energy of level i , respectively.

- (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 ($\Delta J = -1$) of the first overtone vibrational band. (8%)

$$(h = 6.626 \times 10^{-34} \text{ J s}; c = 2.99 \times 10^8 \text{ m s}^{-1}; k_B = 1.3807 \times 10^{-23} \text{ J K}^{-1})$$

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



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_r) can be expressed as

$$U = -N \left(\frac{\partial \ln q}{\partial \beta} \right)_V = N k_B T^2 \left(\frac{\partial q}{\partial T} \right)_V \quad \text{where } \beta = \frac{1}{k_B T}; \quad q_r = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V$$

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 $t = 0$. ($\psi_n(x) = N \sin(n\pi x/a)$, $E_n = n^2\pi^2\hbar^2/(2ma^2)$)
- Write down the wavefunction $\Psi(x, t)$ at time t in terms of $\psi_1(x)$ and $\psi_2(x)$. (5%)
 - Calculate the normalization constant N . (5%)
 - Calculate the expectation value of the energy $\langle E \rangle$ in the state $\Psi(x, t)$ above. (5%)
 - 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%)