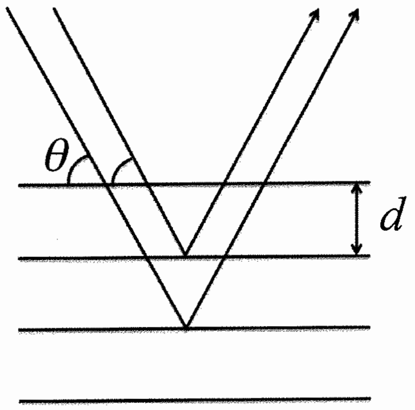
Physical Chemistry I

When the binding energy of an electron is smaller than the energy of irradiated X-ray, an electron is emitted from its atomic orbital as a photoelectron and a hole is left. When a hole is produced in an inner-shell orbital, it is filled by an electron from an outer-shell orbital and the energy equivalent to the energetic difference between two orbitals is emitted as X-ray. Since the wavelength of X-ray emitted by this process is characteristic to the elements, one can identify the kinds of elements.

Analyzing crystals are used for the spectroscopic measurements of emitted X-ray. Consider the reflection of two parallel rays of the same wavelength by two adjacent planes of a lattice of analyzing crystal (Figure). When the path-length difference is an integer number of wavelengths ($n\lambda$) at a certain glancing angle (θ), the reflected waves are in phase and interfere constructively. As a result, a reflection peak appears and the wavelength of X-ray can be determined.



Answer the following questions. Numerical answers should have two significant figures. Show the calculation processes. Use the values of the light speed c (3.0×10^{8} m s^{-1}) and the Planck constant h (6.6×10^{-34} J s). Use the relationships of 1 eV = 1.6×10^{-19} J, sin 35° = 0.57, sin 70° = 0.94, sin 55° = 0.82, and sin 110° = 0.94, if necessary.

I－a

Answer the name of the emitted X-ray.

I－b

Consider $K\alpha_1$ line of Cr atom. Cr $K\alpha_1$ line is emitted by the transition of an electron from L-shell ($2p_{3/2}$) to K-shell (1s). The binding energies of these orbitals are 575 and 5989 eV, respectively. Find the energy of Cr $K\alpha_1$ line in keV.

I－c

Find the wavelength of Cr $K\alpha_1$ line in nm.

I－d

Express the path-length difference ($n\lambda$) using the spacing between the layers (d) and the glancing angle (θ).

I－e

Answer the name of the relationship in I－d.

I－f

Cr Kα_1 line shows the first-order (n = 1) peak at 2θ = 70° by using the LiF(200) analyzing crystal having d of 0.20 nm. Find the wavelength of Cr Kα_1 line in nm.

I－g

Si Kα line shows the first-order (n = 1) peak at 2θ = 110° by using the polyethylene terephthalate (102) analyzing crystal having d of 0.44 nm. Find the wavelength and energy of Si Kα line in nm and keV, respectively.

I－h

LiF(200) analyzing crystal is used for the identification of elements having larger atomic numbers compared to K atom. Describe the reason why the poly(ethylene terephthalate) (102) analyzing crystal is used for the identification of Si atom.

Physical Chemistry II

II-a

Fill in the blanks [①] to [⑥] with appropriate words, phrases, numbers, or formulae.

We first consider an ideal gas A whose amount is n_A (in units of mol) on the basis of thermodynamics. The volume of A is reversibly changed at a constant temperature T_A. The small work done on A, dW, during an infinitesimal volume change in A, dV, is expressed using dV and P_A (the pressure of A) as [①]. Thus, when the volume of A is reversibly changed from V_{A1} to V_{A2}, the work done on A, W_{12}, is given by using the gas constant R, n_A, T_A, V_{A1}, and V_{A2} as follows: [②].

The free energy of A changes due to the work W_{12}. By using the internal energy U, the entropy S, and the temperature T, the Helmholtz free energy F is given as $F = U - TS$. When the amount of A is kept constant, the internal energy depends only on the temperature. Thus, the entropy change in A, ΔS_{12}, due to the foregoing volume change from V_{A1} to V_{A2} is given by [③].

Next, let us consider the above-noted thermodynamic process on the basis of statistical mechanics. By using the number of distinguishable states Ω, the entropy S is given as $S = k \log_e \Omega$. Here, k is the [④] constant, and e is the base of the natural logarithm. k is rewritten using R and the Avogadro constant N_A as $k =$ [⑤].

When the number of distinguishable states of the ideal gas A, Ω_A, is counted, the particles of A are indistinguishable. For comparison purposes, we here consider a fictitious ideal gas, A', whose particles are distinguishable. The number of particles of A, N, is the same as that of A'. When the number of distinguishable states of A' is defined as $\Omega_{A'}$, Ω_A is given by using N as $\Omega_A =$ [⑥]$\cdot\Omega_{A'}$. Thus, the partition function of A, Q_A, is given by

$$Q_A = \boxed{⑥} \cdot \left(\sum_j e^{-\frac{\varepsilon_j}{kT_A}} \right)^N = \boxed{⑥} \cdot q_A^N . \qquad \text{(i)}$$

ε_j in Eq. (i) is an energy level, and $q_A = V_A(2\pi h^{-2} mkT_A)^{3/2}$ is the individual atomic partition function. Here, h is the Planck constant, m is the mass of the particle of A, and V_A is the volume of A.

II-b

By using Q_A, the entropy of A, S_A, is given as

$$S_A = \left(\frac{\partial k T_A \log_e Q_A}{\partial T_A} \right)_{V_A} . \qquad \text{(ii)}$$

Derive the following equation using Eqs. (i) and (ii):

$$S_A = k \log_e\left[\frac{1}{N!} q_A^N\right] + \frac{3}{2} Nk \,. \qquad \text{(iii)}$$

II-c

Using Eq. (iii), calculate S_A (in units of J K^{-1}) at $q_A = 6.0\times10^{30}$ and $N = 6.0\times10^{23}$. Use the following approximations for the calculation: R = 8.3 J K^{-1} mol^{-1}, N_A = 6.0×10^{23} mol^{-1}, $\log_e 10$ = 2.3, and $N! \sim (N/e)^N$.

II-d

By using Eq. (iii), derive an equation for the entropy change ΔS_{12} when the volume of A is changed from V_{A1} to V_{A2} at a constant temperature T_A. Confirm that the derived equation for ΔS_{12} is the same as ③ in II-a when the amount of A is n_A.