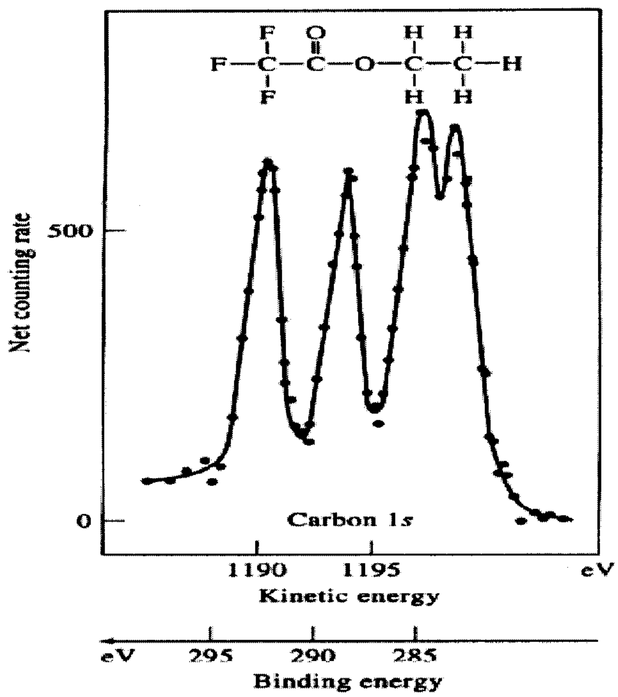
2008 Spring Analytical Chemistry Qualification Exam
(answers can be in either Chinese or English)

1. Explain the ESCA spectrum of Trifluoroacetate shown on the right (10%)



2. (a) Describe the mechanism of the production of MNN Auger electron;
   (b) Describe how it is possible to distinguish between the ESCA peaks from the Auger electron peaks in an ESCA spectrum. (20%)

3. (a) How does Scanning Electron Microscope work?
   (b) Describe principles of two major types of SEM detectors (20%)

4. The acid-base indicator HIn undergoes the following reaction in dilute aqueous solution: $HIn \leftrightarrow H^+ + In^-$

   The following absorbance data were obtained for a 5.00×10^{-4} M solution of HIn in 0.1 M NaOH and 0.1 M HCl. Measurements were made at wavelengths of 485 nm and 625 nm with 1.00-cm cells.

0.1 M NaOH	$A_{485} = 0.075$	$A_{625} = 0.904$
0.1 M HCI	$A_{485} = 0.487$	$A_{625} = 0.181$

   In the NaOH solution, essentially all of the indicator is present as In^-; in the acidic solution, it is essentially all in the form of HIn.
   (a) Calculate molar absorptivities for In^- and HIn at 485 and 625 nm.
   (b) Calculate the acid dissociation constant for the indicator if a pH 5.00 buffer containing a small amount of the indicator exhibits an absorbance of 0.567 at 485 nm and 0.395 at 625 nm (1.00-cm cells).

2008 Qualification examine of Chemical Reaction Engineering

Undergraduate part

4. Titanium dioxide is a wide-band gap semiconductor that is showing promise as an insulating dielectric in VLSI capacitors and for use in solar cells. Thin films of TiO_2 are to be prepared by chemical vapor deposition (CVD) from gaseous titanium tetraisopropoxide (*TTIP*). The overall reaction is

$$Ti(OC_3H_7)_4 \rightarrow TiO_{2(g)} + 4C_3H_6 + 2H_2O$$

The reaction mechanism in a CVD reactor is believed to be

$$TTIP_{(g)} + TTIP_{(g)} \Leftrightarrow I + P_1$$

$$I + S \Leftrightarrow I \cdot S$$

$$I \cdot S \rightarrow TiO_2 + P_2,$$

where I is an active intermediate and P_1 is one set of reaction products (e.g., H_2O, C_3H_6) and P_2 is another set. Assuming the homogeneous gas-phase reaction for *TTIP* is in equilibrium, derive a rate law for the deposition of TiO_2. The experimental results show that at 200℃ the reaction is second order at low partial pressures of *TTIP* and zero order at high partial pressures, while at 300℃ the reaction is second order in *TTIP* over the entire pressure range. Discuss these results in light of the rate law you derived. (20%)

5. The reaction $A \rightarrow B$ is to be carried out isothermally in a continuous-flow reactor. Calculate both the CSTR and PFR reactor volumes necessary to consume 99% of A (i.e., C_A = 0.01 C_{A0}) when the entering molar flow rate is 5 *mol/h*, assuming the reaction rate $-r_A$ is :

(a) $-r_A = k$ with $k = 0.05 \dfrac{mol}{h \cdot dm^3}$

(b) $-r_A = kC_A$ with $k = 0.0001 s^{-1}$

(c) $-r_A = kC_A^2$ with $k = 3 \dfrac{dm^3}{mol \cdot h}$

The entering volumetric flow rate is 10 dm^3/h. (15%)

6. In order to study the photochemical decay of aqueous bromine in bright sunlight, a small quantity of liquid bromine was dissolved in water contained in a glass battery jar and placed in direct sunlight. The following data were obtained at 25℃ :

Time (min)	10	20	30	40	50	60
ppm Br_2	2.45	1.74	1.23	0.88	0.62	0.44

(a) Determine whether the reaction rate is zero, first, or second order in bromine, and calculate the reaction rate constant in units of your choice.

(b) Assuming identical exposure conditions, calculate the required hourly rate of injection of bromine (in pounds) into a sunlit body of water, 25000 gal in volume, in order to maintain a sterilizing level of bromine of 1.0 ppm.

(c) What experimental conditions would you suggest if you were to obtain more data?

(15%)