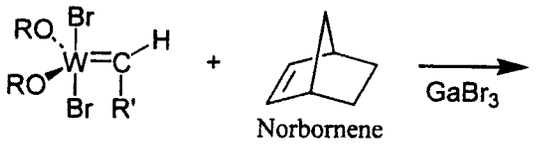
Part I: Inorganic Chemistry (total points: 50)

(1) At low temperature and pressure, a gas-phase reaction can occur between iron atom and toluene. The product, a rather unstable sandwich compound, reacts with ethylene to give compound **X**. Compound **X** decomposed at room temperature to liberate ethylene; at –20°C it reacts with $P(OCH_3)_3$ to give Fe(toluene)$[P(OCH_3)_3]_2$. Suggest a structure for compound **X**. (5%)

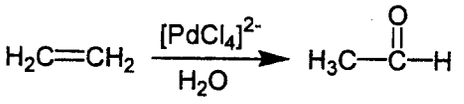
(2) Olefin metathesis involves the formal exchange of methylene ($:CH_2$) fragments between alkenes. Give the products for metathesis between two molecules of formula $H_2C{=}CH_2$ and HRC=CHR. (5%)

(3) An interesting variation on olefin metathesis is the use of carbene complexes to catalyze alkene polymerization, also via a metallacyclobutane intermediate. Give the structure of product polymer for the following polymerization. (5%)



(4) Sketch the molecular orbital diagram for FHF^-. (5%)

(5) The Waker process, used to synthesis acetaldehyde from ethylene, involves a catalytic cycle using $PdCl_4^{2-}$. Propose a cyclic mechanism for this process. (10%)



(6) Determine the point groups of the flowing molecules. (10%)

(a) XeF_4　(b) $PtCl_4^{2-}$　(c) $P(C_6H_5)_3$　(d) ferrocene　(e) $Ru(NH_2CH_2CH_2NH_2)_3^{2+}$

(7) Using the angular overlap model, determine the splitting pattern of *d* orbitals for a tetrahedral complex of formula MX_4, where X is a ligand that can act as σ donor and π donor. (10%)

本試題是否可以使用計算機：☑可使用 ，☐不可使用　（請命題老師勾選）

Part II: Analytical Chemistry (Total points: 50)

(1) Before determining the amount of Na_2CO_3 in an unknown sample, a student decides to check her procedure by analyzing a sample known to contain 98.76% w/w Na_2CO_3. Five replicate determinations of the %w/w Na_2CO_3 in the standard were made with the following results 98.71% 98.59% 98.62% 98.44% 98.58%, and the standard deviation is 0.097%. Is the mean for these five trials significantly different from the accepted value at the 95% confidence level? (10%)

Values of Students's *t* at the 95% confidence level

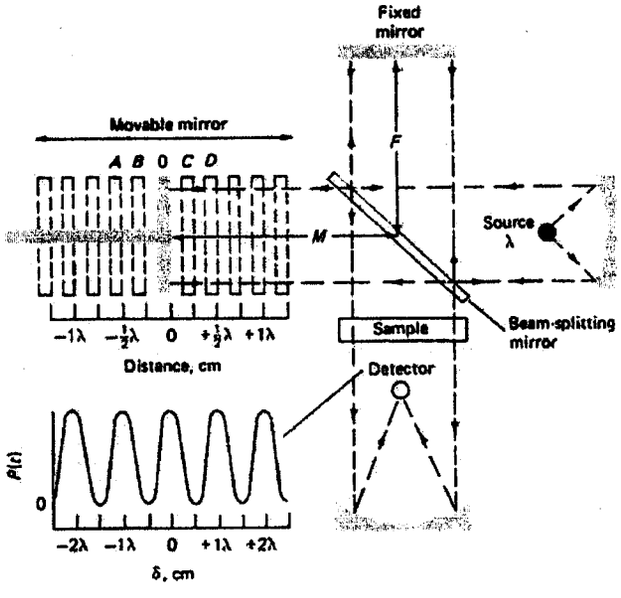
Degree of freedom	2	3	4	5	6	7
t	4.30	3.18	2.78	2.57	2.45	2.36

(2) (a) The opposite figure shows the schematic representation of a Michelson interferometer. Show that the relationship between the optical frequency of the radiation (υ) and the frequency of the interferogram (f) is: (7%)

$$f = \frac{2v_M}{c}\upsilon$$

where v_M is the constant velocity of the mirror and c is the velocity of light. $2(M–F)$ in the figure is termed the *retardation* δ, and λ is the wavelength of the source light.

(b) Calculate the frequency range of a modulated signal from a Michelson interferometer with a mirror velocity of 0.15 cm/s for visible radiation of 700 nm and infrared radiation of 16 μm. (3%)



(3) When ion-selective electrodes are used, it is important that the composition of the standard solution closely approximates the composition of the unknown. For complex or unknown matrixes, the standard addition method can be used. The graphical procedure is based on the equation for the response of the ion-selective electrode, which we will write in the form

$$E = k + \beta\left(\frac{RT\ln 10}{nF}\right)\log[\mathrm{X}]$$

where E is the meter reading in volts and [X] is the concentration of analyte. This reading is the difference in potential of the ion-selective electrode and the reference electrode. The constant k and β depend on the particular ion-selective electrode. n is the charge of the analyte ion (Note that it could be positive or negative). The factor $(RT/F)\ln 10$ is 0.0592 at 298.15 K. If β = 1, then the response is Nernstian. The term $(\beta RT/nF)\ln 10$ is abbreviated as S. Let the initial volume of unknown be V_0 and initial concentration of analyte be c_X. Let the volume of added standard be V_S and the concentration of standard be c_S. Derive the following equation: (10%)

$$(V_0 + V_S)10^{E/S} = 10^{k/S}V_0c_X + 10^{k/S}c_SV_S$$

(4) H_2S from cigarette smoke was collected by bubbling smoke through aqueous NaOH and measured with a sulfide ion-selective electrode. Standard additions of volume V_S containing Na_2S at concentration c_S = 1.78 mM were then made to V_0 = 25.0 mL of unknown and the electrode response, E was measured and listed in the Table. From a separate calibration curve, it was found that β = 0.985 in Equation (A). T = 298.15 K and n = –2 (the charge of S^{2-}). Using the derived equation in problem (3), a graph of $(V_0 + V_S)10^{E/S}$ on the y-axis versus V_S on the x-axis gives a line of y = 0.7448 x + 0.4392. Use the given data to find the concentration of sulfide in the unknown. (10%)

V_S (mL)	E (V)
0	0.0465
1.00	0.0407
2.00	0.0344
3.00	0.0300
4.00	0.0265

(5) Acid-base indicators are themselves acids or bases. Consider an indicator, HIn, which dissociates according to the equation

$$HIn \overset{K_a}{\rightleftarrows} H^+ + In^-$$

The molar absorptivity, ε, is 2080 $M^{-1}cm^{-1}$ for HIn and 14200 $M^{-1}cm^{-1}$ for In^-, at a wavelength of 440 nm.

(a) Write an expression for the absorbance of a solution containing HIn at a concentration [HIn] and In^- at a concentration [In^-] in a cell of pathlength 1.00 cm. The total absorbance is the sum of absorbances of each component. (5%)

(b) A solution containing indicator at a formal concentration of 1.84×10^{-4} M is adjusted to pH 6.23 and found to exhibit an absorbance of 0.868 at 440 nm. Calculate pK_a for this indicator. (5%)