(a) Suggest a rate law consistent with the experimental data.
(b) Suggest a reaction mechanism and rate-limiting step consistent with the rate law. (*Hint*: Some species might be weakly adsorbed).
(c) Determine the catalyst weight necessary to achieve 90% conversion for an entering molar flow of pure butan-2-ol of 10 mol/min at a temperature of 490°C and an entering pressure of 10 atm. $W_{\text{MAX}} - {}^{-}25$.kg
(d) Plot the rate of reaction as a function of conversion.
(e) Repeat part (c) accounting for pressure drop and $\alpha = 0.03\ \text{kg}^{-1}$. Plot P/P_0 and X as a function of catalyst weight down the reactor.

P6-10$_A$ Vanadium oxides are of interest for various sensor applications owing to the sharp metal-insulator transitions they undergo as a function of temperature, pressure or stress. Vanadium tri-isopropoxide (VTIPO) was used to grow vanadium oxide films by **Chemical Vapor Deposition** (*J. Electrochemical Soc. 136*, p. 897 (1989)). The deposition rate as a function of VTIPO pressure is given below for two different temperatures:

$T = 120°\text{C}$

Growth Rate (μm/hr)	0.004	0.015	0.03	0.06	0.085	0.16
VTIPO Pressure (Torr)	0.1	0.2	0.3	0.5	0.7	1.1

$T = 200°\text{C}$

Growth Rate (μm/hr)	1.8	2.8	7.1
VTIPO Pressure (Torr)	0.4	0.5	0.8

In light of the material presented in this chapter, analyze the data and describe your results.

P6-11$_A$ 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** from gaseous titanium tetraisopropoxide (TTIP). The overall reaction is

$$Ti(OC_3H_7)_4 \longrightarrow TiO_2 + 4C_3H_6 + 2H_2O$$

The reaction mechanism in a CVD reactor is believed to be (K. L. Siefering and G. L. Griffin, *J. Electrochemical Soc.*,)

$$TTIP(g) + TTIP(g) \leftrightarrows I + P_1$$

$$I + S \rightleftarrows I{\cdot}S$$

$$I{\cdot}S \longrightarrow TiO_2 + P_2$$

where I is active Intermediate and P_1 is one set reaction of products 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°C the reaction is second-order at low partial pressures of TTIP and zero-order at high partial pressures, while at 300°C the reaction is second-order in TTIP over the entire pressure range. Discuss these results in light of the rate law you derived.

P6-12$_B$ The **Chemical Vapor Deposition** of high-quality silicon dio[illegible] was achieved

Torr and temperatures between 120°C
determined from plots of the data for
a. Molar Ratio $O_2:SiH_4 = 11:1$ Runs

Deposition rate (Å/min)	10	100
Total Pressure (Torr)	2	2.5

b. Total Pressure = 3 Torr

Deposition rate (Å/min)	0	50	80
O_2 Partial Pressure (Torr)	0	0.15	0

c. Molar Ratio $O_2:SiH_4 = 8:1$ Runs

Deposition rate (Å/min)	40	60
% Silane	2%	3%

d. For a fixed total pressure, the dep
as the molar ratio of O_2 to SiH
maximum occurs at a ratio of 10
for a total pressure 760 Torr. Sug
experimental data.

P6-13$_B$ Silicon dioxide is formed by chemica
(DCS) and nitrous oxide (*Proceedi*
Chemical Engineering, Tokyo, p. 2

$$SiH_2Cl_2(g) + 2N_2O(g) \longrightarrow$$

At 900°C the rate of deposition is

$$r''_{SiO_2} = kP_{DCS}P^{0.65}_{N_2O}(\text{Ångstroms/}$$

$$k = 7.1 \times 10^{-3}\ [(\text{Å/min})(\text{milliTorr})$$

The deposition rate is independent

Partial Pressure DCS (mT)	168	168
Partial Pressure N_2O (mT)	340	500
Deposition rate (Å/min)	60	77

(1) Can the reaction order w.r.t. N_2
means than powers that the au
law and evaluate the paramete
(2) Suggest a mechanism and rate-
imental observation.
(3) The wafers are 0.125 meters in
of the reactor. Silicon dioxide
the wafers. The reactor diamet
20 mm a This arrangeme
area of 2. ^{2} per m^3 of react

Suggest a rate law consistent with the experimental data.
Suggest a reaction mechanism and rate-limiting step consistent with the rate law. (*Hint*: Some species might be weakly adsorbed).
Determine the catalyst weight necessary to achieve 90% conversion for an entering molar flow of pure butan-2-ol of 10 mol/min at a temperature of 490°C and an entering pressure of 10 atm. $W_{MAX} - {}^{-}25$.kg
Plot the rate of reaction as a function of conversion.
Repeat part (c) accounting for pressure drop and $\alpha = 0.03\ \text{kg}^{-1}$. Plot P/P_0 and X as a function of catalyst weight down the reactor.

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VTIPO Pressure (Torr)	0.1	0.2	0.3	0.5	0.7	1.1

$T = 200°\text{C}$

Growth Rate (μm/hr)	1.8	2.8	7.1
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$$I + S \rightleftarrows I{\cdot}S$$

$$I{\cdot}S \longrightarrow TiO_2 + P_2$$

re I is active Intermediate and P_1 is one set reaction of products and another set. Assuming the homogeneous gas-phase reaction for TTIP equilibrium, derive a rate law for the deposition of TiO_2. The experıtal results show that at 200°C the reaction is second-order at low partial sures of TTIP and zero-order at high partial pressures, while at 300°C eaction is second-order in TTIP over the entire pressure range. Discuss e results in light of the rate law you derived.

Chemical Vapor Deposition of high-quality silicon dioxide was achieved eacting silane and oxygen (*J. Electrochemical Soc. 134*, No. 10 p. 2517 7)). The deposition was carried out at pressures ranging from 2 to 12 Torr and temperatures between 120°C and 300°C. The following data were determined from plots of the data for runs at 250°C.

a. Molar Ratio $O_2{:}SiH_4 = 11{:}1$ Runs 1 through 5

Deposition rate (Å/min)	10	100	110	60	40
Total Pressure (Torr)	2	2.5	3.5	6	7

b. Total Pressure = 3 Torr

Deposition rate (Å/min)	0	50	80	100	100	80	50	30	0
O_2 Partial Pressure (Torr)	0	0.15	0.2	0.5	0.9	1.5	2.0	2.2	2.4

c. Molar Ratio $O_2{:}SiH_4 = 8{:}1$ Runs 7 through 9

Deposition rate (Å/min)	40	60	80
% Silane	2%	3%	4%

d. For a fixed total pressure, the deposition rate goes through a maximum as the molar ratio of O_2 to SiH_4 is increased from zero to 90. This maximum occurs at a ratio of 10 at a total pressure 3 Torr and at 1.5 for a total pressure 760 Torr. Suggest a mechanism consistent with the experimental data.

P6-13$_B$ Silicon dioxide is formed by chemical vapor deposition from dichlorosilane (DCS) and nitrous oxide (*Proceedings of the Third World Congress of Chemical Engineering*, Tokyo, p. 290 (1986)).

$$SiH_2Cl_2(g) + 2N_2O(g) \longrightarrow SiO_2(s) + 2N_2(g) + 2HCl(g)$$

At 900°C the rate of deposition is

$$r''_{SiO_2} = kP_{DCS}P_{N_2O}^{0.65}(\text{Ångstroms/minute}),\ \text{with } P_i \text{ in milliTorr (mT)}$$

$$k = 7.1 \times 10^{-3}\ [(\text{Å/min})(\text{milliTorr})^{-1.65}]$$

$$= 3.12 \times 10^{-8}\ \frac{\text{gmol}}{\text{m}^2\text{min}}\ (\text{mT})^{-1.65}$$

The deposition rate is independent of HCl and nitrogen. At 900°C

Partial Pressure DCS (mT)	168	168	168	168	80	115	165	210
Partial Pressure N_2O (mT)	340	500	750	900	426	426	426	426
Deposition rate (Å/min)	60	77.5	100	110	29	42	60	75

(1) Can the reaction order w.r.t. N_2O and DCS be explained by some other means than powers that the author used? If so, formulate a new rate law and evaluate the parameters.

(2) Suggest a mechanism and rate-limiting step(s) consistent with experimental observation.

(3) The wafers are 0.125 meters in diameter and set upright along the length of the reactor. Silicon dioxide is deposited uniformly on both sides of the wafers. The reactor diameter is 250 mm and the wafers are spaced 20 mm apart. This arrangement corresponds to a deposition surface area of 250 m² per m³ of reactor volume. Assume that the gas phase behaves as a plug-flow reactor at steady state. Develop the equations for the axial deposition profile. Specifically determine the thickness of the deposited film at 900°C on the 1st, 50th and 110th wafers in the reactor after 30 minutes. Dichlorosilane is fed at a partial pressure of 157 milliTorr and a rate of 0.00368 mol/min while Nitrous Oxide is fed at a partial pressure of 447 milliTorr and a rate of 0.013 mol/min.

P6-14$_C$ The following data for the hydrogenation of *i*-octene to form *i*-octane were obtained using a differential reactor operated at 200°C.

		Partial Pressure (atm)		
Run	*Rate* (mol/g·h)	*Hydrogen*	*i-Octene*	*i-Octane*
1	0.0362	1	1	0
2	0.0239	1	1	1
3	0.0390	3	1	1
4	0.0351	1	3	1
5	0.0114	1	1	3
6	0.0534	10	1	0
7	0.0280	1	10	0
8	0.0033	1	1	10
9	0.0380	2	2	2
10	0.0090	1	1	4
11	0.0127	0.6	0.6	0.6
12	0.0566	5	5	5

(a) Develop a rate law and evaluate all the rate law parameters.

(b) Suggest a mechanism consistent with the experimental data. Hydrogen and *i*-octene are to be fed in stoichiometric proportions at a total rate of 5 mol/min at 200°C and 3 atm.

(c) Neglecting pressure drop, calculate the catalyst weight necessary to achieve 80% conversion of *i*-octane in a CSTR and in a plug-flow reactor.

(d) If pressure drop is taken into account and the $\frac{1}{8}$-in. catalyst pellets are packed in $1\frac{1}{2}$-in. schedule 80 pipes 35 ft long, what catalyst weight is necessary to achieve 80% conversion? The void fraction is 40% and the density of the catalyst is 2.6 g/cm^3.

P6-15$_B$*N* The use of a differential reactor to study the formation of methane from hydrogen and carbon monoxide over a nickel catalyst gave the following:

$$r'_{\mathrm{CH_4}} = \frac{0.0183 P_{\mathrm{H_2}}^{1/2} P_{\mathrm{CO}}}{1 + 1.5 P_{\mathrm{H_2}}} \text{ mol/g cat}\cdot\text{s}$$

Suggest a mechanism and rate-limiting step that is consistent with the experimental observation.

It is desired to produce 20 tons/day of CH_4. Calculate the catalyst weights necessary to achieve 80% conversion in:

(a) A fixed-bed.

(b) A fluidized-bed.

The feed consists of 75% H_2 and 25% CO at a temperature of 500°F and a pressure of 10 atm. Assume both molecular and atomic hydrogen are adsorbed on the surface.