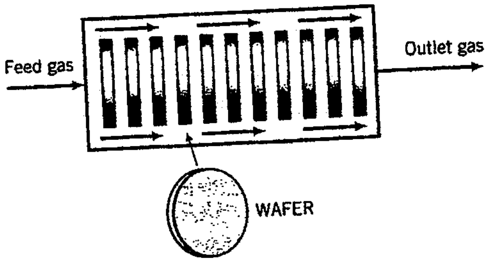
5.34.[15] In *chemical vapor deposition* (CVD), a semiconducting or insulating solid material is formed in a reaction between a gaseous species and a species adsorbed on the surface of silicon *wafers* (disks about 10 cm in diameter and 1 mm thick). The coated wafers are subjected to further processing to produce the microelectronic chips in computers and most other electronic devices in use today.

In one such process, silicon dioxide (MW = 60.06, SG = 2.67) is formed in the reaction between gaseous dichlorosilane (DCS) and adsorbed nitrous oxide:

$$SiH_2\overset{a}{Cl_2}(g) + 2N_2\overset{b}{O}(ads) \longrightarrow SiO_2(s) + \overset{c}{2N_2}(g) + \overset{d}{2HCl}(g)$$

A mixture of DCS and N_2O flows through a "boat reactor"—a horizontal pipe in which 50–100 silicon wafers about 12 cm in diameter and 1 mm thick are set upright along the reactor length, with about 20 mm separation between each wafer. A side view of the reactor is shown below:



The feed gas enters the reactor at a rate of 3.74 SCMM (standard cubic meters per minute) and contains 22.0 mole% DCS and the balance N_2O. In the reactor, the gas flows around the wafers, DCS and N_2O diffuse into the spaces between the wafers, N_2O is adsorbed on the wafer surfaces, and the adsorbed N_2O reacts with gaseous DCS. The silicon dioxide formed remains on the surface, and the nitrogen and hydrogen chloride go into the gas phase and eventually leave the reactor with the unconsumed reactants. The temperature and absolute pressure in the reactor are constant at 900°C and 604 millitorr.

(a) The percentage conversion of DCS at a certain axial position (distance along the length of the reactor) is 60%. Calculate the volumetric flow rate (m^3/min) of gas at this axial position.

(b) The rate of deposition of silicon dioxide per unit area of wafer surface is given by the formula

$$r\left(\frac{\text{mol SiO}_2}{\text{m}^2\cdot\text{s}}\right) = 3.16 \times 10^{-8} p_{DCS}\, p_{N_2O}^{0.65}$$

where p_{DCS} and p_{N_2O} are the partial pressures of DCS and N_2O in millitorr. What is r at the axial position in the reactor where the DCS conversion is 60%?

(c) Consider a wafer located at the axial position determined in part (b). How thick is the silicon dioxide layer on that wafer after two hours of reactor operation, assuming that gas diffusion is rapid enough at the low reactor pressure for the composition of the gas (and hence the component partial pressures) to be uniform over the wafer surface? Express your answer in angstroms, where 1 Å = 1.0×10^{-10} m. (*Hint:* You can calculate the rate of growth of the SiO_2 layer in Å/min from r and properties of SiO_2 given in the problem statement.) Would the thickness be greater or less than this value at an axial position closer to the reactor entrance? Briefly explain your answer.

5.35. A gas turbine power plant receives a shipment of hydrocarbon fuel whose composition is uncertain but may be represented by the expression C_xH_y. The fuel is burned with excess air. An analysis of the product gas gives the following results on a moisture-free basis: 10.5%(v/v) CO_2, 5.3% O_2, and 84.2% N_2.

(a) Determine the molar ratio of hydrogen to carbon in the fuel (r), where $r = y/x$, and the percentage excess air used in the combustion.

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[15] Based on a problem in H. S. Fogler, *Elements of Chemical Reaction Engineering*, 2nd Edition, Prentice Hall, Englewood Cliffs, NJ, 1992, p. 323.

[redacted]

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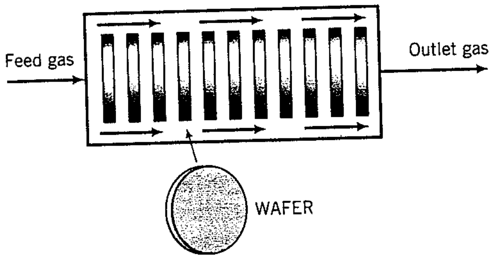

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(a) Determine the molar ratio of hydrogen to carbon in the fuel (r), where $r = y/x$, and the percentage excess air used in the combustion.

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[15] Based on a problem in H. S. Fogler, *Elements of Chemical Reaction Engineering*, 2nd Edition, Prentice Hall, Englewood Cliffs, NJ, 1992, p. 323.

For liquids
$C_A = C_{A0}(1-X)$
$C_B = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
Therefore, for a given rate law we have
$-r_A = g(X)$

Then

$$C_A = \frac{F_{A0}}{v_0}(1-X) = C_{A0}(1-X) \qquad \text{(3-29)}$$

$$C_B = C_{A0}\left(\Theta_B - \frac{b}{a}X\right) \quad \text{etc.}$$

However, for gas-phase reactions the volumetric flow rate most often changes during the course of the reaction due to a change in the total number of moles or in temperature or pressure. One cannot always use Equation (3-29) to express concentration as a function of conversion for gas-phase reactions.

3.3.4 Volume Change with Reaction

In our previous discussions, we considered primarily systems in which the reaction volume or volumetric flow rate did not vary as the reaction progressed. Most batch and liquid-phase and some gas-phase systems fall into this category. There are other systems, though, in which either V or v do vary, and these will now be considered.

A situation in which a varying flow rate occurs quite frequently is in gas-phase reactions that do not have an equal number of product and reactant moles. For example, in the synthesis of ammonia,

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

4 mol of reactants gives 2 mol of product. In flow systems where this type of reaction occurs, the molar flow rate will be changing as the reaction progresses. Because only equal numbers of moles occupy equal volumes in the gas phase at the same temperature and pressure, the volumetric flow rate will also change.

Another variable-volume situation, which occurs much less frequently, is in batch reactors where volume changes with time. Examples of this situation are the combustion chamber of the internal-combustion engine and the expanding gases within the breech and barrel of a firearm as it is fired.

In the stoichiometric tables presented on the preceding pages, it was not necessary to make assumptions concerning a volume change in the first four columns of the table (i.e., the species, initial number of moles or molar feed rate, change within the reactor, and the remaining number of moles or the molar effluent rate). All of these columns of the stoichiometric table are independent of the volume or density and they are *identical* for constant-volume (constant-density) and varying-volume (varying-density) situations. Only when concentration is expressed as a function of conversion does variable density enter the picture.

Individual concentrations can be determined by expressing the volume V for a batch system (or volumetric flow rate v for a flow system) as a function of conversion using the following equation of state:

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w system) as a function

Equation of state

$$PV = ZN_T RT \tag{3-30}$$

in which V and N_T are defined as before and

T = temperature, K
P = total pressure, atm (kPa; 1 atm = 101.3 kPa)
Z = compressibility factor
R = gas constant = 0.08206 dm$^3\cdot$atm/g mol$\cdot$K

This equation is valid at any point in the system at any time t. At time $t = 0$ (i.e., when the reaction is initiated), Equation (3-30) becomes

$$P_0 V_0 = Z_0 N_{T0} R T_0 \tag{3-31}$$

Dividing Equation (3-30) by Equation (3-31) and rearranging yields

$$V = V_0 \left(\frac{P_0}{P}\right) \frac{T}{T_0} \left(\frac{Z}{Z_0}\right) \frac{N_T}{N_{T0}} \tag{3-32}$$

We now want to express the volume V as a function of the conversion X. Recalling the equation for the total number of moles in Table 3-2,

$$N_T = N_{T0} + \delta N_{A0} X \tag{3-33}$$

we divide through by N_{T0}:

$$\frac{N_T}{N_{T0}} = 1 + \frac{N_{A0}}{N_{T0}} \delta X = 1 + \delta y_{A0} X \tag{3-34}$$

where y_{A0} is the mole fraction of A initially present. If all the species in the generalized reaction are in the gas phase, then

$$\boxed{\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1} \tag{3-23}$$

Equation (3-34) is further simplified by letting

$$\varepsilon = \frac{\text{change in total number of moles for complete conversion}}{\text{total number of moles fed to the reactor}}$$

Definitions of δ and ε

In symbols,

$$\varepsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right) \frac{N_{A0}}{N_{T0}} = y_{A0}\delta \tag{3-35}$$

$$\boxed{\varepsilon = y_{A0}\delta} \tag{3-36}$$

Equation (3-32) now becomes

$$V = V_0\left(\frac{P_0}{P}\right)\frac{T}{T_0}\left(\frac{Z}{Z_0}\right)(1+\varepsilon X) \tag{3-37}$$

In gas-phase systems that we shall be studying, the temperatures and pressures are such that the compressibility factor will not change significantly during the course of the reaction; hence $Z_0 \cong Z$. For a batch system the volume of gas at any time t is

Volume of gas for
a variable volume
batch reaction

$$\boxed{V = V_0\left(\frac{P_0}{P}\right)(1+\varepsilon X)\,\frac{T}{T_0}} \tag{3-38}$$

Equation (3-38) applies only to a *variable-volume* batch reactor. If the reactor is a rigid steel container of constant volume, then of course $V = V_0$. For a constant-volume container, $V = V_0$, and Equation (3-38) can be used to calculate the pressure inside the reactor as a function of temperature and conversion.

An expression similar to Equation (3-38) for a variable-volume batch reactor exists for a variable-volume flow system. To derive the concentrations of the species in terms of conversion for a variable-volume flow system, we shall use the relationships for the total concentration. The total concentration at any point in the reactor is

$$C_T = \frac{F_T}{v} = \frac{P}{ZRT} \tag{3-39}$$

At the entrance to the reactor,

$$C_{T0} = \frac{F_{T0}}{v_0} = \frac{P_0}{Z_0RT_0} \tag{3-40}$$

Taking the ratio of Equation (3-40) to Equation (3-39) and assuming negligible changes in the compressibility factor, we have upon rearrangement

$$\boxed{v = v_0\left(\frac{F_T}{F_{T0}}\right)\frac{P_0}{P}\left(\frac{T}{T_0}\right)} \tag{3-41}$$

From Table 3-3, the total molar flow rate is

$$F_T = F_{T0} + F_{A0}\,\delta X \tag{3-42}$$

Substituting for F_T in Equation (3-41) gives

$$\begin{aligned} v &= v_0\frac{F_{T0}+F_{A0}\,\delta X}{F_{T0}}\left(\frac{P_0}{P}\right)\frac{T}{T_0} \\ &= v_0\left(1+\frac{F_{A0}}{F_{T0}}\,\delta X\right)\frac{P_0}{P}\left(\frac{T}{T_0}\right) = v_0(1+y_{A0}\,\delta X)\,\frac{P_0}{P}\left(\frac{T}{T_0}\right) \end{aligned} \tag{3-43}$$

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$$\delta X)\,\frac{P_0}{P}\left(\frac{T}{T_0}\right)$$

Gas-phase volumetric flow rate

$$\boxed{v = v_0(1+\varepsilon X)\,\frac{P_0}{P}\left(\frac{T}{T_0}\right)} \tag{3-44}$$

We can now express the concentration of species j for a flow system in terms of conversion:

$$C_j = \frac{F_j}{v} = \frac{F_j}{v_0\left(\dfrac{F_T}{F_{T0}}\,\dfrac{P_0}{P}\,\dfrac{T}{T_0}\right)} = \left(\frac{F_{T0}}{v_0}\right)\left(\frac{F_j}{F_T}\right)\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

For multiple reactions (Chapter 6)

$$\boxed{C_j = C_{T0}\left(\frac{F_j}{F_T}\right)\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)} \tag{3-45}$$

We will use this form of the concentration equation for multiple gas-phase reactions and for membrane reactors. Substituting for F_j and F_T in terms of conversion in Equation (3-45) yields

$$C_j = C_{T0}\,\frac{F_{A0}(\Theta_j + \nu_j X)}{F_{T0} + F_{A0}\delta X}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

Dividing numerator and denominator by F_{T0}, we have

$$C_j = C_{T0}\left(\frac{F_{A0}}{F_{T0}}\right)\frac{\Theta_j + \nu_i X}{1 + (F_{A0}/F_{T0})\,\delta X}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

Recalling $y_{A0} = F_{A0}/F_{T0}$ and $C_{A0} = y_{A0}C_{T0}$, then

Gas-phase concentration as a function of conversion

$$\boxed{C_j = \frac{C_{A0}(\Theta_j + \nu_j X)}{1 + \varepsilon X}\left(\frac{P}{P_0}\right)\frac{T_0}{T}} \tag{3-46}$$

where ν_i is the stoichiometric coefficient, which is negative for reactants and positive for products. For example, for the reaction

$$\mathrm{A} + \frac{b}{a}\,\mathrm{B} \longrightarrow \frac{c}{a}\,\mathrm{C} + \frac{d}{a}\,\mathrm{D} \tag{2-2}$$

$\nu_A = -1$, $\nu_B = -b/a$, $\nu_C = c/a$, and $\nu_D = d/a$.

The stoichiometry table for the gas-phase reaction (2-2) is given in Table 3-4.

TABLE 3-4. CONCENTRATIONS IN A VARIABLE-VOLUME GAS FLOW SYSTEM

$$\begin{aligned}
C_A &= \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} &&= \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0} &&= C_{A0}\left(\frac{1-X}{1+\varepsilon X}\right)\frac{T_0}{T}\left(\frac{P}{P_0}\right)\\
C_B &= \frac{F_B}{v} = \frac{F_{A0}[\Theta_B-(b/a)X]}{v} &&= \frac{F_{A0}[\Theta_B-(b/a)X]}{v_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0} &&= C_{A0}\left(\frac{\Theta_B-(b/a)X}{1+\varepsilon X}\right)\frac{T_0}{T}\left(\frac{P}{P_0}\right)\\
C_C &= \frac{F_C}{v} = \frac{F_{A0}[\Theta_C+(c/a)X]}{v} &&= \frac{F_{A0}[\Theta_C+(c/a)X]}{v_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0} &&= C_{A0}\left(\frac{\Theta_C+(c/a)X}{1+\varepsilon X}\right)\frac{T_0}{T}\left(\frac{P}{P_0}\right)\\
C_D &= \frac{F_D}{v} = \frac{F_{A0}[\Theta_D+(d/a)X]}{v} &&= \frac{F_{A0}[\Theta_D+(d/a)X]}{v_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0} &&= C_{A0}\left(\frac{\Theta_D+(d/a)X}{1+\varepsilon X}\right)\frac{T_0}{T}\left(\frac{P}{P_0}\right)\\
C_I &= \frac{F_I}{v} = \frac{F_{A0}\Theta_I}{v} &&= \frac{F_{A0}\Theta_I}{v_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0} &&= \frac{C_{A0}\Theta_I}{1+\varepsilon X}\left(\frac{T_0}{T}\right)\frac{P}{P_0}
\end{aligned}$$

At last! We now have $C_j = h_j(X)$ and $-r_A = g(X)$ for variable-volume gas-phase reactions

Example 3–6 Manipulation of the Equation for $C_j = h_j\,(X)$

Show under what conditions and manipulation the expression for C_B for a gas flow system reduces to that given in Table 3-4.

Solution

For a flow system the concentration is *defined* as

$$C_B = \frac{F_B}{v} \tag{E3-6.1}$$

From Table 3-3, the molar flow rate and conversion are related by

$$F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right) \tag{E3-6.2}$$

Combining Equations (E3-6.1) and (E3-6.2) yields

$$C_B = \frac{F_{A0}[\Theta_B-(b/a)X]}{v} \tag{E3-6.3}$$

This equation for v is only for a gas-phase reaction

Using Equation (3-44) gives us

$$v = v_0(1+\varepsilon X)\,\frac{P_0}{P}\left(\frac{T}{T_0}\right) \tag{3-44}$$

to substitute for the volumetric flow rate gives

$$C_B = \frac{F_B}{v} = \frac{F_{A0}[\Theta_B-(b/a)X]}{v_0(1+\varepsilon X)}\left(\frac{P}{P_0}\right)\frac{T_0}{T} \tag{E3-6.4}$$

Recalling $\dfrac{F_{A0}}{v_0} = C_{A0}$, we obtain

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