8 Exercises

1. (a) For each of the following systems, determine the values of C and of R, and a proper set of chemical equations in conventional canonical form. List the component species and the noncomponent species separately.

   i. $\{(P_2I_4, P_4, H_2O, PH_4I, H_3PO_4), (P, I, H, O)\}$(Carrano, 1978).

   ii. $\{(O_2, (CH_3)_3COH, CO_2, H_2O, CH_3COCH_3, CH_3COOH), (O, C, H)\}$, relating to the oxidation of *t*-butyl alchohol (Missen, 1970).

   iii. $\{(OH^-, O_2, e^-, H_2O, O_3), (H, O, p)\}$, relating to the reduction half reaction for ozone (Olson, 1997).

   iv. $\{(CH_4, O_2, CO_2, H_2O, CO, H_2, N_2), (C, O, H, N_2)\}$, relating to the partial combustion of CH_4 with *air*; *cf.* Example 7.

   v. $\{(C(gr), CO(g), CO_2(g), Zn(g), Zn(l), ZnO(s)), (C, O, Zn)\}$, relating to the production of zinc metal (Denbigh, 1981, pp. 191-193).

   vi. $\{([Cr(N_2H_4CO)_6]_4[Cr(CN)_6]_3, KMnO_4, H_2SO_4, K_2Cr_2O_7, MnSO_4, CO_2, KNO_3, K_2SO_4, H_2O), (Cr, N, H, C, O, K, Mn, S)\}$, described as an "incredibly challenging" redox system (Stout, 1995).

   vii. $\{(O_2(g), H_2O(g), CH_4(g), CO(g), CO_2(g), H_2(g), N_2(g), CHO(g), CH_2O(g), OH(g), Fe(s), FeO(s), Fe_3O_4(s), C(gr), CaO(s), CaCO_3(s)), (O, H, C, Fe, Ca, N_2)\}$, a blast furnace system (Madeley and Toguri, 1973a, 1973b).

   viii. $\{(Fe(C_2O_4)^+, Fe(C_2O_4)_2{}^-, Fe(C_2O_4)_3{}^{3-}, Fe^{3+}, SO_4{}^{2-}, HSO_4{}^-, H^+, HC_2O_4{}^-, H_2C_2O_4, C_2O_4{}^{2-}), (C, Fe, H, O, S, p)\}$ (Swinnerton and Miller, 1959).

   ix. $\{(CH_4, CH_3D, CH_2D_2, CHD_3, CD_4), (C, H, D)\}$, relating to isotopic exchange among the deuteromethanes (Apse and Missen, 1967).

   x. $\{(C_2H_4, C_3H_6, C_4H_8, C_5H_{10}, C_6H_{12}), (C, H)\}$, relating to the oligomerization of C_2H_4.

   xi. $\{(H_2O(l), C_2H_6O(l), C_2H_4O_2(l), C_4H_8O_2(l), H_2O(g), C_2H_6O(g), C_2H_4O_2(g), C_4,H_8O_2(g), (C_2H_4O_2)_2(g)), (C, H, O)\}$, relating to the liquid-vapor esterification of ethyl alchohol with acetic acid, and allowing for the presence of acetic acid dimer in the vapor phase (Sanderson and Chien,1973).

xii. {(O_2, H_2O, H_2SO_4, $KMnO_4$, H_2O_2, K_2SO_4, $MnSO_4$), (O, H, S, K, Mn)} (Missen and Smith,1990).

(b) For each system in (a), change the order of the species and the order of the elements, and repeat.

2. (a) For a system of N species and $rank(\mathbf{A}) = C$, what is the apparent maximum number of proper sets of chemical equations in canonical form?

   (b) Under what circumstances would the actual number of proper sets in canonical form be less than the apparent maximum number in (a)?

   (c) How would the actual number be determined, if it is less than the apparent maximum number?

   (d) For the system in Example 2, what is the number of proper sets of chemical equations in canonical form?

3. For the system in Example 9, Segraves and Wickersham (1991) wrote the chemical equation

$$\begin{aligned} 10NH_4ClO_4 &= 2.5Cl_2 + 2N_2O + 2.5NOCl + 1.5HCl + 19.25H_2O \\ &\quad +1.75N_2 + 7.125O_2 + ClO_2 \qquad \text{(A)} \end{aligned}$$

   They noted, however, that “different...conditions could make almost any overall decomposition possible...there is no one overall decomposition reaction...” In comparison with the result given in Example 9, what are the implications of writing a single equation such as (A)? Explain.

4. The system in Exercise 1.(a)xii is the basis for “wet” chemical analysis for H_2O_2 in aqueous solution. The stoichiometry in this case is expressed by the chemical equation

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2 \quad (B)$$

   In comparison with the result obtained in Exercise 1.(a)xii, what is the implication of writing (B)? (Missen and Smith, 1990).

5. In section 2.5 of the tutorial, it is noted that a proper set of chemical equations for a reacting system is not unique, and that any one equation of the set may be replaced by an equation obtained by taking a non-zero multiple of it and adding a linear combination of the remaining equations, to form a different proper set. For the system in Example 2, replace the set of equations (4), (5), and (6) by (4a) = (4) + (5), (5a) = (4) + (6), and (6a) = (5) + 3(6). Is the set (4a), (5a), and (6a) a proper set of chemical equations? Explain.

6. McBride and Adams(1984) give the following (skeletal) reaction for the production of perchloric acid from ammonium perchlorate:

$$
\begin{aligned}
NH_4ClO_4 + HNO_3 + HCl + H_2O \quad \rightarrow \quad & HClO_4 \cdot 2H_2O + N_2O + NO \\
& + NO_2 + Cl_2
\end{aligned}
$$

They state that "The equation(*sic*) has been left unbalanced because no solution that has ever been produced satisfies the observed results. It is quite an exercise to balance it at all." What is the answer to this apparent dilemma? (Their statement has also been discussed by Jensen, 1987).

7. Ferguson(1996) has posed the problem of balancing the following skeletal reaction to his High School chemistry students:

$$KClO_3 + HCl \rightarrow KCl + H_2O + Cl_2 + ClO_2$$

After giving a table of many sets of coefficients for achieving this, and indicating that more exist, he concluded that the correct answer is

$$2KClO_3 + 4HCl \rightarrow 2KCl + 2H_2O + Cl_2 + 2ClO_2$$

This results from his reasoning that, in addition to atom-balances, "transfer of electrons...needs to be balanced," thus requiring an excursion into consideration of balancing redox reactions. Is Ferguson's reasoning correct? Explain quantitatively.

8. In a kinetics investigation of the vapor-phase oxidation of CH_4 over a certain catalyst in a differential flow reactor, Spencer and Pereira (1987) obtained a reaction network consisting of two steps in series, in which CH_4 first oxidizes to HCHO, followed by further oxidation

of HCHO to CO, together with a third step in parallel in which CH_4 oxidizes to CO_2:

$$
\begin{aligned}
CH_4 + O_2 &\rightarrow HCHO + H_2O \\
HCHO + \frac{1}{2}O_2 &\rightarrow CO + H_2O \\
CH_4 + 2O_2 &\rightarrow CO_2 + 2H_2O
\end{aligned}
$$

(a) Does this reaction network correspond stoichiometrically to a proper set of chemical equations? Justify your answer.

(b) What is the minimum number of species whose concentrations must be measured, so that the concentrations of all other species may be calculated? Explain.

(c) What is the minimum number of species reaction rates, r_i, from which all other species rates can be calculated? Relate all other species rates to a particular chosen minimum set. What is the most efficacious way of choosing a minimum set?
(Based on examples given by Missen *et al.*, 1999, Chapter 5.)

9. In a kinetics investigation of the catalytic vapor-phase oxidation of benzene (with *air*) to maleic anhydride ($C_4H_2O_3$) in a flow reactor, Vaidyanathan and Doraiswamy(1968) stated that the "reaction scheme...may be stoichiometrically represented as":

$$
\begin{aligned}
C_6H_6 + \frac{9}{2}O_2 &\rightarrow C_4H_2O_3 + 2CO_2 + 2H_2O \\
C_4H_2O_3 + 3O_2 &\rightarrow 4CO_2 + H_2O \\
C_6H_6 + \frac{15}{2}O_2 &\rightarrow 6CO_2 + 3H_2O
\end{aligned}
$$

(a) Is a corresponding set of three chemical *equations* a proper set? Justify your answer. Is the first of these an allowable equation?

(b) The authors used partial pressure (p_i) as a measure of concentration. They reported p_i for 4 species. How many of these are independent as a minimum set? Choosing a set of this number of species and their p_i, relate the partial pressures of *all* other species to these p_i.

(c) Similarly, what is a minimum set of species reaction rates r_i? Relate all other species rates to a particular chosen minimum set. (Based on a problem given by Missen *et al.* (1999), chapter 5.)

10. A possible free-radical chain mechanism for the thermal decomposition of acetaldehyde (to CH_4 and CO) is the Rice-Herzfeld mechanism (Laidler and Liu, 1967):

$$\begin{aligned} CH_3CHO &\rightarrow CH_3^\bullet + CHO^\bullet &(1)\\ CHO^\bullet &\rightarrow CO + H^\bullet &(2)\\ H^\bullet + CH_3CHO &\rightarrow CH_3CO^\bullet + H_2 &(3)\\ CH_3^\bullet + CH_3CHO &\rightarrow CH_4 + CH_3CO^\bullet &(4)\\ CH_3CO^\bullet &\rightarrow CH_3^\bullet + CO &(5)\\ 2CH_3^\bullet &\rightarrow C_2H_6 &(6) \end{aligned}$$

Find a kinetics scheme for each of the following cases:

(a) H_2 and C_2H_6, in addition to the free radical species, are *minor* species.

(b) H_2 and C_2H_6 , but not the free radical species, are *major* species.

11. The first step in the extraction of Ti from titania (TiO_2) may be the chlorination of the oxide to produce the tetrachloride, in the absence of carbon to lower the partial pressure of O_2. Kubashewski and Alcock (1979) give equilibrium data in the form of ΔG^0 for three reactions as follows:

$$\begin{aligned} C(s) + \frac{1}{2}O_2(g) &= CO(g);\ \ \Delta G_1^0 = -111,700 - 87.65T &(7)\\ C(s) + O_2(g) &= CO_2(g);\ \ \Delta G_2^0 = -394,100 - 0.84T &(8)\\ TiO_2(s) + 2Cl_2(g) &= TiCl_4(g) + O_2(g); &(9)\\ & \Delta G_3^0 = 161,100 - 56.5T &(10) \end{aligned}$$

where ΔG^0 is in J and T is in K. Using these data, obtain a consistent set of the standard chemical potentials (μ^0) of the species at 1000K; *i.e.*, for the species in the system represented by {(O_2, H_2O, H_2SO_4, $KMnO_4$, H_2O_2, K_2SO_4, $MnSO_4$), (O, H, S, K, Mn)}.