

Chemical Equilibrium

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Summary:

In this handout, we provide a complete and generic method for finding the chemical equilibrium of an arbitrary system of reactions. We then provide four example problems and example code.

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I. CALCULATING THE EQUILIBRIUM COEFFICIENT FROM PHYSICAL PROPERTIES

A. Given information:

1. Thermodynamic state of system

temperature T
pressure p

2. Reaction Stoichiometry

$\underline{\nu}$ where $\nu_{i,j}$ is the stoichiometric coefficient of species j in reaction i .

$\nu_{i,j} > 0$ for products, $\nu_{i,j} < 0$ for reactants, $\nu_{i,j} = 0$ if species j is not involved in reaction i

$\underline{\nu}$ is an $n_r \times n_c$ matrix where n_r is the number of reactions and n_c is the number of chemical species

The stoichiometric coefficient matrix must be for a complete and independent set of reactions.

3. Given the Gibbs Free Energy of Formation and the Enthalpy of Formation at reference temperature

Gibbs Free Energy of Formation at reference temperature $\underline{\Delta G_f}(T_{ref})$

Enthalpy of Formation at reference temperature $\underline{\Delta H_f}(T_{ref})$

These properties are given for common materials in the CRC Handbook of Chemistry and Physics.

4. Given Heat Capacity Polynomial Fit

$$C_{p,j}(T) = a + bT + cT^2 + dT^3$$

The constant are given for common materials in various references and texts, e.g. Sandler.

B. Enthalpy of formation at an arbitrary temperature

In general:

$$\Delta H_{f,j}(T) = \Delta H_{f,j}(T_{ref}) + \int_{T_{ref}}^T C_{p,j}(T) dT \quad (1)$$

For the formulation of the heat capacity given above:

$$\Delta H_{f,j}(T) = \Delta H_{f,j}(T_{ref}) + \int_{T_{ref}}^T (a + bT + cT^2 + dT^3) dT \quad (2.a)$$

$$\Delta H_{f,j}(T) = \Delta H_{f,j}(T_{\text{ref}}) + \left[aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 + \frac{d}{4}T^4 \right]_{T_{\text{ref}}}^T \quad (2.b)$$

$$\Delta H_{f,j}(T) = \Delta H_{f,j}(T_{\text{ref}}) + \left[aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 + \frac{d}{4}T^4 \right] - \left[aT_{\text{ref}} + \frac{b}{2}T_{\text{ref}}^2 + \frac{c}{3}T_{\text{ref}}^3 + \frac{d}{4}T_{\text{ref}}^4 \right] \quad (2.c)$$

C. Free Energy of formation at an arbitrary temperature

We need the temperature dependence of $\Delta G_{f,j}(T)$. The Gibbs-Helmholtz equation tells us that if we know the enthalpy then we know the temperature dependence of the free energy.

$$\left(\frac{d \left[\frac{\Delta G_{f,j}(T)}{T} \right]}{dT} \right)_p = -\frac{\Delta H_{f,j}(T)}{T^2} \quad (3)$$

Aside: The Gibbs-Helmholtz relation can be proved as follows:

$$\left(\frac{d \left[\frac{\Delta G(T)}{T} \right]}{dT} \right)_p = \left[\frac{1}{T} \left(\frac{d\Delta G(T)}{dT} \right)_p - \frac{\Delta G(T)}{T^2} \right] \quad (4.a)$$

Substitute $\Delta G(T) = \Delta H(T) - T\Delta S(T)$ and $\left(\frac{d\Delta G(T)}{dT} \right)_p = -\Delta S$, so

$$\left(\frac{d \left[\frac{\Delta G(T)}{T} \right]}{dT} \right)_p = \left[-\frac{\Delta S(T)}{T} - \frac{\Delta H(T) - T\Delta S(T)}{T^2} \right] = -\frac{\Delta H(T)}{T^2} \quad (4.b)$$

Therefore, using the Gibbs-Helmholtz relation (equation (3)), we can express the Free Energy of formation at an arbitrary temperature as:

$$\int_{T_{\text{ref}}}^T d \left[\frac{\Delta G_{f,j}(T)}{T} \right] = \int_{T_{\text{ref}}}^T -\frac{\Delta H_{f,j}(T)}{T^2} dT \quad (5.a)$$

$$\frac{\Delta G_{f,j}(T)}{T} - \frac{\Delta G_{f,j}(T_{\text{ref}})}{T_{\text{ref}}} = \int_{T_{\text{ref}}}^T -\frac{\Delta H_{f,j}(T)}{T^2} dT \quad (5.b)$$

$$\Delta G_{f,j}(T) = T \frac{\Delta G_{f,j}(T_{\text{ref}})}{T_{\text{ref}}} - T \int_{T_{\text{ref}}}^T \frac{\Delta H_{f,j}(T)}{T^2} dT \quad (5.c)$$

For our form of the Enthalpy of formation, given in equation (2.c), we have:

$$\Delta G_{f,j}(T) = T \frac{\Delta G_{f,j}(T_{\text{ref}})}{T_{\text{ref}}} - T \int_{T_{\text{ref}}}^T \frac{\Delta H_{f,j}(T_{\text{ref}}) + \left[aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 + \frac{d}{4}T^4 \right] - \left[aT_{\text{ref}} + \frac{b}{2}T_{\text{ref}}^2 + \frac{c}{3}T_{\text{ref}}^3 + \frac{d}{4}T_{\text{ref}}^4 \right]}{T^2} dT$$

$$\begin{aligned} \Delta G_{f,j}(T) &= \frac{T}{T_{\text{ref}}} \Delta G_{f,j}(T_{\text{ref}}) - T \int_{T_{\text{ref}}}^T \frac{\Delta H_{f,j}(T_{\text{ref}}) - \left[aT_{\text{ref}} + \frac{b}{2}T_{\text{ref}}^2 + \frac{c}{3}T_{\text{ref}}^3 + \frac{d}{4}T_{\text{ref}}^4 \right]}{T^2} dT \\ &= \frac{T}{T_{\text{ref}}} \Delta G_{f,j}(T_{\text{ref}}) - T \int_{T_{\text{ref}}}^T \left(a \frac{1}{T} + \frac{b}{2} + \frac{c}{3}T + \frac{d}{4}T^2 \right) dT \end{aligned} \quad (6.b)$$

$$\begin{aligned} \Delta G_{f,j}(T) &= \frac{T}{T_{\text{ref}}} \Delta G_{f,j}(T_{\text{ref}}) + \left\{ \Delta H_{f,j}(T_{\text{ref}}) - \left[aT_{\text{ref}} + \frac{b}{2}T_{\text{ref}}^2 + \frac{c}{3}T_{\text{ref}}^3 + \frac{d}{4}T_{\text{ref}}^4 \right] \right\} \left[1 - \frac{T}{T_{\text{ref}}} \right] \\ &\quad - T \left[\left(a \ln(T) + \frac{b}{2}T + \frac{c}{6}T^2 + \frac{d}{12}T^3 \right) - \left(a \ln(T_{\text{ref}}) + \frac{b}{2}T_{\text{ref}} + \frac{c}{6}T_{\text{ref}}^2 + \frac{d}{12}T_{\text{ref}}^3 \right) \right] \end{aligned} \quad (6.c)$$

You can check that when $T = T_{\text{ref}}$, the left hand side of equation (6c) is equal to $\Delta G_{f,j}(T_{\text{ref}})$.

D. Free Energy and Enthalpy of Formation of reaction at any arbitrary temperature

Explicitly

$$\Delta G_{r,i}(T) = \sum_{j=1}^{n_c} \nu_{i,j} \Delta G_{f,j}(T) \quad \text{and} \quad \Delta H_{r,i}(T) = \sum_{j=1}^{n_c} \nu_{i,j} \Delta H_{f,j}(T) \quad (7)$$

In matrix notation:

$$\underline{\Delta G_r}(T) = \underline{\nu} \underline{\Delta G_f}(T) \quad \text{and} \quad \underline{\Delta H_r}(T) = \underline{\nu} \underline{\Delta H_f}(T) \quad (8)$$

E. Equilibrium Constant at an arbitrary temperature

$$K_i(T) = \exp\left[-\frac{\Delta G_{r,i}(T)}{RT}\right] \quad (9)$$

Aside: It should be pointed out that people frequently relate the temperature dependence of an equilibrium coefficient to the enthalpy of reaction using the van't Hoff isochore.

$$\left(\frac{d[\ln K_i]}{dT}\right)_p = \frac{\Delta H_{r,i}(T)}{RT^2} \quad (10)$$

It should be noted that we performed an equivalent operation, but have taken the steps in a more natural and intuitive order.

Aside: It should also be pointed out that people frequently write:

$$K_i(T) = K_i(T_{\text{ref}}) \exp\left[-\frac{\Delta H_{r,i}(T_{\text{ref}})}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right] \quad (11)$$

This is an unnecessary approximation of the derivation performed above, because it assumes that $\Delta H_{r,i}(T)$ is not a function of temperature.

II. CALCULATING THE EQUILIBRIUM COEFFICIENT FROM EXTENTS OF REACTION

We can also calculate the equilibrium coefficient from the extents of reaction. This equilibrium coefficient will be the same as the equilibrium coefficient calculated from physical properties. Solving the chemical equilibria problem boils down to finding the extents of reaction and temperature that equate the equilibrium coefficient calculated both ways.

Consider the reaction



with initial mole fractions of each species and moles of each species given by

$$\underline{x}_0 = \begin{bmatrix} x_{A,0} \\ x_{B,0} \\ x_{C,0} \\ x_{D,0} \end{bmatrix} \quad \text{and} \quad \underline{N}_0 = \underline{x}_0 N_0 \quad (13)$$

where N_0 is the initial total number of moles. It should be noted that we assume the stoichiometric coefficients are negative for reactants and positive for products.

If the reaction is an elementary reaction, then the rate of the forward reaction is proportional to the concentration of the reacting species raised to their stoichiometric coefficients.

$$\text{rate}_f = k_f C_A^{|v_A|} C_B^{|v_B|} = k_f \left(\frac{N_A}{V} \right)^{|v_A|} \left(\frac{N_B}{V} \right)^{|v_B|} = k_f \left(\frac{x_A N}{V} \right)^{|v_A|} \left(\frac{x_B N}{V} \right)^{|v_B|} \quad (14.a)$$

and the rate of the reverse reaction has the form:

$$\text{rate}_r = k_r \left(\frac{x_C N}{V} \right)^{|v_C|} \left(\frac{x_D N}{V} \right)^{|v_D|} \quad (14.b)$$

where k_f is the rate constant of the forward reaction and k_r is the rate constant of the reverse reaction, and where N is the total number of moles in the system at equilibrium and V is the reactor volume. We must put absolute value signs on the stoichiometric coefficients since we have defined reactants to have negative stoichiometric coefficients and products to have positive stoichiometric coefficients. The units of the rate constants, k_f and k_r , depend on the particular values of the stoichiometric coefficients. Generally the units of k_f and k_r are determined by the fact that the rates, rate_f and rate_r , have units of moles/volume/time.

At thermodynamic equilibrium, the forward and reverse rates are equal. Therefore:

$$\text{rate}_f = \text{rate}_r \quad (15)$$

$$k_f \left(\frac{A}{V} \right)^{|v_A|} \left(\frac{B}{V} \right)^{|v_B|} = k_r \left(\frac{C}{V} \right)^{|v_C|} \left(\frac{D}{V} \right)^{|v_D|} \quad (16)$$

$$\frac{k_f}{k_r} = \frac{\left(\frac{x_C N}{V}\right)^{|v_C|} \left(\frac{x_D N}{V}\right)^{|v_D|}}{\left(\frac{x_A N}{V}\right)^{|v_A|} \left(\frac{x_B N}{V}\right)^{|v_B|}} = \prod_{j=A}^D \left(\frac{x_j N}{V}\right)^{v_j} \quad (17)$$

Here we have removed the absolute values from the stoichiometric coefficients so the reactants appear in the denominator. We can pull N/V out of the product since it is not a function of i .

$$\frac{k_f}{k_r} = \prod_{j=A}^D \left(\frac{x_j N}{V}\right)^{v_j} = \left(\frac{N}{V}\right)^{\sum_{j=A}^D v_j} \prod_{j=A}^D x_j^{v_j} \quad (18)$$

The equilibrium coefficient, K , is proportional to the ratio of forward to reverse reaction rates. However, K , is

dimensionless, while the ratio of $\frac{k_f}{k_r}$ has units of $\left(\frac{N}{V}\right)^{\sum_{j=A}^D v_j}$, or for example $\left(\frac{\text{moles}}{\text{liter}}\right)^{\sum_{j=A}^D v_j}$. Therefore, we need to include a proportionality constant, in order to make the ratio dimensionless.

$$K = \left(\frac{N}{V}\right)_{\text{ref}}^{-\sum_{j=A}^D v_j} \frac{k_f}{k_r} = \left(\frac{\left(\frac{N}{V}\right)}{\left(\frac{N}{V}\right)_{\text{ref}}}\right)^{\sum_{j=A}^D v_j} \prod_{j=A}^D x_j^{v_j} \quad (19)$$

The reference state is taken at the system temperature.

In the specific example of an ideal gas, $N/V = P^*RT$. In this case, the equilibrium coefficient becomes

$$K = \left(\frac{PRT}{P_{\text{ref}}RT}\right)^{\sum_{j=A}^D v_j} \prod_{j=A}^D x_j^{v_j} = \left(\frac{P}{P_{\text{ref}}}\right)^{\sum_{j=A}^D v_j} \prod_{j=A}^D x_j^{v_j} \quad (20)$$

If we take the reference pressure has a value of 1 of whatever units P is measured in (be it atmosphere, Pascals, bars or mmHg), then P_{ref} disappears from the equation.

Aside: A rigorous derivation of how the equilibrium coefficient can be obtained from mole fractions can be performed taking advantage of the fact that, at equilibrium,

$$\sum_{j=A}^D v_j \mu_j = 0 = \sum_{j=A}^D v_j (G_{f,j} + RT \ln \hat{a}_j) = \sum_{j=A}^D v_j G_{f,j} + \sum_{j=A}^D v_j RT \ln \hat{a}_j \quad (21)$$

where μ_j is the chemical potential of species j , and \hat{a}_j is the activity of species j . The first term on the left hand side of equation (21) can be rewritten using equation (9)

$$\sum_{j=A}^D v_j G_{f,j} = -RT \ln(K) \quad (22)$$

Substituting equation (22) into equation (21) and rearranging for K, yields:

$$K = \prod_{j=A}^D (\hat{a}_j)^{v_j} \quad (23)$$

The activity of species j, \hat{a}_j , can be approximated in a variety of ways depending upon the situation. If we have an ideal gas then:

$$\hat{a}_j = \frac{x_j P}{P_{\text{ref}}} \quad (24)$$

Substituting equation (24) into equation (23) yields equation (20).

$$K = \left(\frac{P}{P_{\text{ref}}} \right)^{\sum_{j=A}^D v_j} \prod_{j=A}^D x_j^{v_j} \quad \text{for ideal gases} \quad (20.b)$$

If we have an incompressible liquid with molar density that is constant, regardless of composition then we have equation (19). If we choose our reference density to be this constant density then equation (19) becomes:

$$K = \prod_{j=A}^D x_j^{v_j} \quad \text{for ideal, incompressible liquids} \quad (25)$$

Other assumptions, provide different forms of the activity coefficient. For nonideal gases, we have

$$K = \prod_{j=A}^D \hat{f}_j^{v_j} \quad \text{for nonideal gases} \quad (20.c)$$

Regardless of which of the formulations of the equilibrium coefficient employed, we need to find the mole fractions, \underline{X} , which give the same value of the equilibrium coefficient as was obtained above from the physical properties. In the case of our general reaction given in equation (12) we have four mole fractions, and thus four unknowns. If we have four unknowns we need four equations, which we could then solve numerically. However, it is practically much more difficult to solve four nonlinear algebraic equations for four unknowns than it is to solve one nonlinear algebraic equation for one unknown. For this reason, we introduce an extent of reaction, χ . By using the extent of reaction, we reduce the number of unknowns to one, namely χ , regardless of how many species are in the system.

The extent of reaction, χ , defines how far the reaction has proceeded. We can write the extent of reaction in terms of moles or as a dimensionless quantity. Here, we will define the extent of reaction in units of moles. The extent of reaction is the number of moles generated for an imaginary product with a stoichiometric coefficient of

one. Thus for our reaction above, for an arbitrary value of χ , we would have consumed/produced $v_j\chi$ moles of component j.

Rigorously the extent of reaction is defined as

$$\chi(t) \equiv V \int_{t_0}^t (\text{rate}_f - \text{rate}_r) dt \quad (26)$$

Equation (26) is a mathematical expression describing the total number of moles of a species with $v_j = 1$ produced by the combined forward and reverse reaction over a time period ranging from t_0 to t . Equation (26) has units of moles.

The extent of reaction is a bounded variable. You cannot react more than the limiting reactant allows. The maximum value of the extent of reaction is determined by the limiting reactant.

$$\chi_{\max} = \max\left(\frac{N_{A,0}}{v_A}, \frac{N_{B,0}}{v_B}\right) \quad (27.a)$$

The minimum value of the extent of reaction is determined by the limiting product.

$$\chi_{\min} = \min\left(\frac{N_{C,0}}{v_C}, \frac{N_{D,0}}{v_D}\right) \quad (27.b)$$

In the event that there is no product initially in the system, equation (14.b) returns a minimum value of zero.

At thermodynamic equilibrium, time = infinity, so the extent of reaction is given by:

$$\chi(t_\infty) \equiv V \int_{t_0}^{t_\infty} (\text{rate}_f - \text{rate}_r) dt \equiv \chi \quad (28)$$

At this point, we need to relate the mole fractions to the extent of reaction. We write mole balances for each species.

$$\text{accumulation} = \text{in} - \text{out} + \text{generation} - \text{consumption} \quad (29)$$

The units of the mole balance (and every term in the mole balance) are moles per time. For an arbitrary species j, we have

$$\frac{dN_j}{dt} = F_{\text{in}}x_{j,\text{in}} - F_{\text{out}}x_j + v_j V \text{rate}_f - v_j V \text{rate}_r \quad (30)$$

If we integrate this mole balance from time 0 (our initial state) to time infinity (where we have thermodynamic equilibrium), then we have:

$$\int_{N_{j,0}}^{N_j} dN_j = \int_{t_0}^{t_\infty} (F_{in}x_{j,in} - F_{out}x_j + v_j Vrate_f - v_j Vrate_r) dt \quad (31)$$

$$N_j - N_{j,0} = \int_{t_0}^{t_\infty} F_{in}x_{j,in} dt - \int_{t_0}^{t_\infty} F_{out}x_j dt + v_j \int_{t_0}^{t_\infty} (Vrate_f - Vrate_r) dt \quad (32)$$

This last term is the definition of the extent of reaction multiplied by the stoichiometric coefficient.

$$N_j - N_{j,0} = \int_{t_0}^{t_\infty} F_{in}x_{j,in} dt - \int_{t_0}^{t_\infty} F_{out}x_j dt + v_j \chi \quad (33)$$

To further simplify equation (33), then we need to make some assumptions about our system. If the system is a batch reactor, then we have no in or out terms, and equation (33) becomes:

$$N_j = N_{j,0} + v_j \chi \quad \text{for batch reactors only} \quad (34)$$

Equation (34) simply states that the number of moles of j in the system at thermodynamic equilibrium is equal to the initial number plus the amount generated or consumed by the reaction. We can write equation (34) for all species in the reaction.

We can obtain mole fractions as follows:

$$x_j = \frac{N_j}{N} = \frac{N_{j,0} + v_j \chi}{N} \quad (35)$$

where N is the total number of moles at thermodynamic equilibrium, given by:

$$N = \sum_{j=A}^D N_j = \sum_{j=A}^D (N_{j,0} + v_j \chi) \quad (36)$$

Equation (35) is important. It tells us that, if we know the extent of reaction, we know all the mole fractions. If we take the case of ideal gases and we substitute equation (35) into equation (20.b),

$$K = \left(\frac{P}{P_{ref}} \right)^{\sum_{j=A}^D v_j} \prod_{j=A}^D x_j^{v_j} \quad \text{for ideal gases} \quad (20.b)$$

$$K = \left(\frac{P}{P_{ref}} \right)^{\sum_{j=A}^D v_j} \prod_{j=A}^D \left(\frac{N_{j,0} + v_j \chi}{\sum_{k=A}^D (N_{k,0} + v_k \chi)} \right)^{v_j} \quad \text{for ideal gases} \quad (37)$$

then we have one equation and one unknown, χ .

If, instead of a batch reactor, we have a continuous stirred tank reactor (CSTR), then the mole balance has in and out terms, which are not zero. Starting again with the generic mole balance, equation (29), we assume that the contents of the reactor at any given instant are at thermodynamic equilibrium.

$$0 = F_{in}x_{j,in} - F_{out}x_j + v_j V rate_f - v_j V rate_r \quad (38)$$

We again integrate this equation. Since we are at steady state, the inlet and outlet terms are constant

$$0 = \int_{t_0}^{t_\infty} F_{in}x_{j,in} dt - \int_{t_0}^{t_\infty} F_{out}x_j dt + v_j \chi \quad (39)$$

Since we are at steady state, the inlet and outlet terms are constant and can be pulled from the integral.

$$F_{out}x_j \Delta t = F_{in}x_{j,in} \Delta t + v_j \chi \quad (40)$$

By selecting our Δt to be in the one unit of whatever time unit the flowrate is given with respect to, (e.g. if F_{in} is given in moles/sec, then $\Delta t = 1$ sec), then $F_{in}x_{j,in} \Delta t = N_{in}x_{j,in} = N_{j,in}$, and we have

$$N_{j,out} = N_{j,in} + v_j \chi \quad \text{for CSTRs} \quad (41)$$

Note that this is the same equation that we had for batch reactors in equation (34), where we have replaced initial and final conditions with inlet and outlet conditions. Therefore, we can proceed as we did with the batch reactor to obtain the equilibrium coefficient.

However, the CSTR introduces an additional unknown, the outlet flowrate, F_{out} . If we have an incompressible liquid then $F_{out} = F_{in}$. If we have an ideal gas, $F_{out} = F_{in}$

Extension to multiple reactions:

We can write the equilibrium coefficient, equation (23), for any arbitrary number of reactions. However, these reactions must form a complete and independent set of reactions for the system. In order to determine a complete and independent set of reactions, you must perform a numerical analysis of the stoichiometric and atomic matrices. (This procedure is outlined as an example in the Linear Algebra notes on the ChE 301 website.)

For reaction i , (assuming an ideal gas mixture and a batch reactor) we write:

$$K_i = \left(\frac{P}{P_{ref}} \right)^{\sum_{j=A}^D v_{i,j}} \prod_{j=A}^D \left(\frac{N_{j,o} + \sum_{i=1}^{n_r} v_{i,j} \chi_i}{\sum_{k=A}^D \left(N_{k,o} + \sum_{i=1}^{n_r} v_{i,k} \chi_i \right)} \right)^{v_{i,j}} \quad (42)$$

where our mole balance yielded moles of the form:

$$N_j = N_{j,o} + \sum_{i=1}^{n_r} v_{i,k} \chi_i \quad (43)$$

and where the mole fraction was given by:

$$x_j = \frac{N_j}{N} = \frac{N_{j,o} + \sum_{i=1}^{n_r} v_{i,j} \chi_i}{\sum_{k=A}^D N_k} = \frac{N_{j,o} + \sum_{i=1}^{n_r} v_{i,j} \chi_i}{\sum_{k=A}^D \left(N_{k,o} + \sum_{i=1}^{n_r} v_{i,k} \chi_i \right)} \quad (44)$$

we have n_r equations of the type given by equation (42) and n_r unknowns, χ_i , from $i = 1$ to n_r .

III. A NUMERICAL ALGORITHM FOR SOLVING THE CHEMICAL EQUILIBRIUM PROBLEM

Our goal is to find the mole fractions that equate the equilibrium coefficient calculated from physical properties (equation (9)) to the equilibrium coefficient calculated from mole fractions, for example (equation (42)) for ideal gases.

$$K_i(T) = \exp\left[-\frac{\Delta G_{r,i}(T)}{RT}\right] \quad (9)$$

$$K_i = \left(\frac{P}{P_{\text{ref}}}\right)^{\sum_{j=A}^D v_{i,j}} \prod_{j=A}^D \left(\frac{N_{j,o} + \sum_{i=1}^{n_r} v_{i,j} \chi_i}{\sum_{k=A}^D \left(N_{k,o} + \sum_{i=1}^{n_r} v_{i,k} \chi_i \right)} \right)^{v_{i,j}} \quad (42)$$

We will distinguish these two formulations of the equilibrium coefficients as K_i^{pp} and K_i^{mf} . The equation we need to solve is then:

$$f_i = K_i^{\text{pp}} - K_i^{\text{mf}} = 0 \quad \text{for } i = 1 \text{ to } n_r. \quad (45)$$

A. Isothermal Case

First assume the reactor is operating at a known, constant temperature. The algorithm to obtain the unknowns, the extents of reactions, is as follows:

1. Obtain needed physical and system properties.
 - a. stoichiometry of a complete and independent set of reactions
 - b. Free Energies of formation at a reference temperature
 - c. Enthalpies of formation at a reference temperature
 - d. Heat Capacity as a function of T
 - e.1. Batch reactors: initial number of moles of each component
 - e.2. CSTRs: feed flowrate and composition of feed
2. Calculate K_i^{pp} from equation (9)
3. Guess extents of reaction, χ_i for $i = 1$ to n_r
4. Calculate K_i^{mf} from equation (42) for $i = 1$ to n_r
5. Evaluate objective functions in equation (45) for $i = 1$ to n_r
6. If values of objective functions are less than a desired tolerance, stop. Otherwise, loop back to step 3., and pick new values of χ_i , using some numerical root-finding technique, e.g. the multivariate Newton-Raphson method.

B. Adiabatic Case

Assume the reactor is operating under adiabatic conditions. Then we have $n_r + 1$ unknowns, where the additional unknown is the temperature of the reactor at thermodynamic equilibrium. In order to solve for this additional unknown, we need an additional equation. The additional equation is an energy balance. The energy balance has the general form:

$$\text{accumulation} = \text{in} - \text{out} + \text{generation} - \text{consumption} \quad (29)$$

$$\frac{dH(T)}{dt} = F_{in}H_{in}(T_{in}) - F_{out}H(T) + V \sum_{i=1}^{n_r} \Delta H_{r,i}(T)(\text{rate}_{f,i} - \text{rate}_{r,i}) \quad (46)$$

The units of this energy balance and every term in the energy balance are energy per time, e.g. J/s. The enthalpies are all given in units of energy per mole. The enthalpy of reaction at an arbitrary temperature is given by equation (7). The other enthalpies need to be determined. For ideal mixtures,

$$H_{in}(T_{in}) = \sum_{j=1}^{n_c} H_{f,j}(T_{in})x_j \quad \text{and} \quad H(T) = \sum_{j=1}^{n_c} H_{f,j}(T)x_j \quad (47)$$

The enthalpies of formation at arbitrary temperatures are given for a general case by equation (1) and for a particular case by equation (2.c). The point is that if we know the temperature and compositions, we know the enthalpies.

If we have a batch reactor, we can integrate this energy balance from the initial time to the thermodynamic infinite time limit, just as we did with the mole balance. Doing so yields

$$H_j(T) - H_{j,o}(T_o) = \sum_{j=1}^{n_c} H_{f,j}(T)x_j \quad \text{for batch reactors only} \quad (48)$$

The additional objective function for the temperature is then:

$$f_{n_r+1} = H_j(T) - H_{j,o}(T_o) - \sum_{j=1}^{n_c} H_{f,j}(T)x_j = 0 \quad (49)$$

For a CSTR, the additional objective function for the temperature is then:

$$f_{n_r+1} = F_{out}H_j(T) - F_{in}H_{j,in}(T_{in}) - \sum_{j=1}^{n_c} H_{f,j}(T)x_j = 0 \quad (50)$$

where the in and out pure component enthalpies are given as:

$$H_j(T) = \int_{T_{\text{ref}}}^T C_{p,j}(T) dT \quad (51)$$

The algorithm to obtain the unknowns, the extents of reactions and the adiabatic temperature, is as follows:

1. Obtain needed physical and system properties.
 - a. stoichiometry of a complete and independent set of reactions
 - b. Free Energies of formation at a reference temperature
 - c. Enthalpies of formation at a reference temperature
 - d. Heat Capacity as a function of T
 - e.1. Batch reactors: initial number of moles of each component
 - e.2. CSTRs: feed flowrate and composition of feed
3. Guess the temperature, and the extents of reaction, χ_i for $i = 1$ to \mathcal{N}_r
2. Calculate K_i^{pp} from equation (9) using the guessed temperature
4. Calculate K_i^{mf} from equation (42) for $i = 1$ to \mathcal{N}_r using the guessed χ_i
5. Calculate mole fractions for all components from equation (44) using the guessed χ_i
6. Evaluate objective functions in equation (45) for $i = 1$ to \mathcal{N}_r
7. Evaluate objective function for temperature in equation (49)
8. If values of objective functions are less than a desired tolerance, stop. Otherwise, loop back to step 3., and pick new values of χ_i and T, using some numerical root-finding technique, e.g. the multivariate Newton-Raphson method.

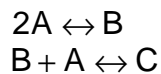
C. Numerical Tricks

Even though we have outlined the algorithm, it is not a simple plug-and-chug problem. The resulting objective functions are highly nonlinear, in both the isothermal and adiabatic cases. You require very good initial guesses to converge to the solution. With a bad initial guess, typically the program simply crashes or does not converge.

How do you get around this?

1. Pick consistent initial guesses.

Make sure your extents of reaction are within the allowable maximum and minimum limits given by equation (27). If a product from reaction 1 is a reactant in reaction 2, then the extent of reaction 2 is limited by your guess at χ_1 . As an example consider the following 2 reactions, a dimerization and trimerization reaction,



Assume the system initially contains 1 mole of A, no B and no C.

The limits on χ_1 are $0 \leq \chi_1 \leq \frac{N_{A,0}}{2}$. The limits of χ_2 are $0 \leq \chi_2 \leq \chi_1$, because you can't use more moles of B in reaction 2 than were generated by reaction 1. Also, you can find additional constraints, $0 \leq \chi_1 + \chi_2 \leq \frac{N_{A,0}}{3}$ because you can't use more A than was initially in the system. Your initial guesses should fall within these constraints. If they do not, then you are in a physically unreasonable starting position and the convergence algorithm is not likely to converge to the physical root.

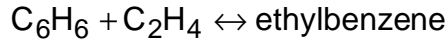
2. *Parameter-Stepping*

Let's say we are solving an isothermal system. If you solve the system at one temperature, then use that converged solution as the initial guess for a slightly higher temperature. Then using that technique, you can obtain solutions easily through the entire temperature range. The best place to start is a temperature where all the χ_i are in the middle of the range. As the χ_i approach their upper and lower limits, the values of the equilibrium coefficients approach 0 and positive infinity, making convergence much more difficult.

We will demonstrate these algorithms and these tricks in the following 2 examples.

IV. EXAMPLE WITH ONE REACTION

Consider the reaction of benzene and ethylene to form ethyl-benzene



We have a batch reactor initially at a pressure of 5 atm and a Temperature, T_0 with 1.0 moles of benzene and 2.0 moles of ethylene.

The matrix of stoichiometric coefficients is given by: (benzene, ethylene, ethyl-benzene)

$$\text{nu} = [-1 \quad -1 \quad 1];$$

The heats of formation at $T_{\text{ref}} = 298.1$ K are (benzene, ethylene, ethyl-benzene) in units of Kcal/mole

$$\text{DHfref} = [19.820; 12.496; 7.120];$$

The heats of formation at $T_{\text{ref}} = 298.1$ K are (benzene, ethylene, ethyl-benzene) in units of Kcal/mole

$$\text{DGfref} = [30.989; 16.282; 31.208];$$

For a heat capacity function of the form (cal/mole/K)

$$C_{p,j}(T) = a + 10^{-2}bT + 10^{-5}cT^2 + 10^{-9}dT^3$$

The constants are (columns = benzene, ethylene, ethyl-benzene, rows = a,b,c,d)

$$\text{Cpcon} = \begin{bmatrix} -8.650 & 0.944 & -8.398 \\ 11.578 & 3.735 & 15.935 \\ -7.540 & -1.993 & -10.003 \\ 18.54 & 4.220 & 23.95 \end{bmatrix};$$

A. Isothermal Case

Find the extent of reaction and composition of the reaction under isothermal conditions, where the initial temperature, T_0 , is the same as the isothermal temperature, T_{ISO} . Do this for the range $450 \text{ K} \leq T_{\text{ISO}} \leq 1600 \text{ K}$.

Using the system of nonlinear algebraic equation solver, `syseqn_all.m`, we are required to create an input file with the objective equations. This input file is given in Appendix A. It performs the calculations given in Part I. and II. of this handout.

To solve only at 1 temperature, say $T_{\text{ISO}} = 900$ K, we simply use `syseqn_all.m`. For help on how to use `syseqn_all.m`, type `help syseqn_all` at the Matlab command line prompt. At the command line prompt, we type:

```
» syseqn_all(1,[0.5]);
```

The first argument, 1, tells syseqn which solution technique to use, in this case method 1, which is the MATLAB intrinsic function fsolve.m. The second argument is a vector of initial guesses. In this case we only have one unknown, so we have only one initial guess, $\chi_1 = 0.5$. The code returns:

```
Attempting solution with MATLABs fsolve function
VARIABLE      INPUT      OUTPUT
      1      5.0000000e-001  5.0989046e-001
```

The program has converged with a value of the extent of reaction: $\chi_1 = 0.5099$. How did I know to try this initial guess? Just trial and error. If we try other initial guesses, we find that some converge to the root and some do not.

I tried a variety of initial guesses until I found one that allowed the code to converge to a reasonable solution. I do not want to perform this trial and error more than once. Now that I have the solution at $T_{\text{ISO}}=900$ K, I will use that as an initial guess for $T_{\text{ISO}}=910$ K. Then I will use that guess for a T_{ISO} ten degrees higher until I reach my upper limit of interest.

I do not want to do all this by hand, so I have written a short code which loops through these temperatures, and updates the initial guess, and finally plots the extent of reaction and the compositions as a function of temperature. The code, chemeq_loop.m is given in Appendix B.

A plot of the extent of reaction as a function of the isothermal temperature is shown in Figure 1. We can see that as the temperature increases, the conversion decreases. This makes sense because, for exothermic reactions, like this one, $\Delta H_{r,i}(T = 500) = -104.5 \frac{\text{kJ}}{\text{mol}}$, increased temperature favors the reactants.

A plot of the mole fractions as a function of the isothermal temperature is shown in Figure 2. At temperatures below 600 K, the reaction proceeds to nearly 100% completion. Our composition in this regime is 50% ethylene (which was present in excess) and 50% ethyl-benzene. At temperatures above 1600 K, there is virtually no reaction. We have 2/3 ethylene and 1/3 benzene as was our initial condition.

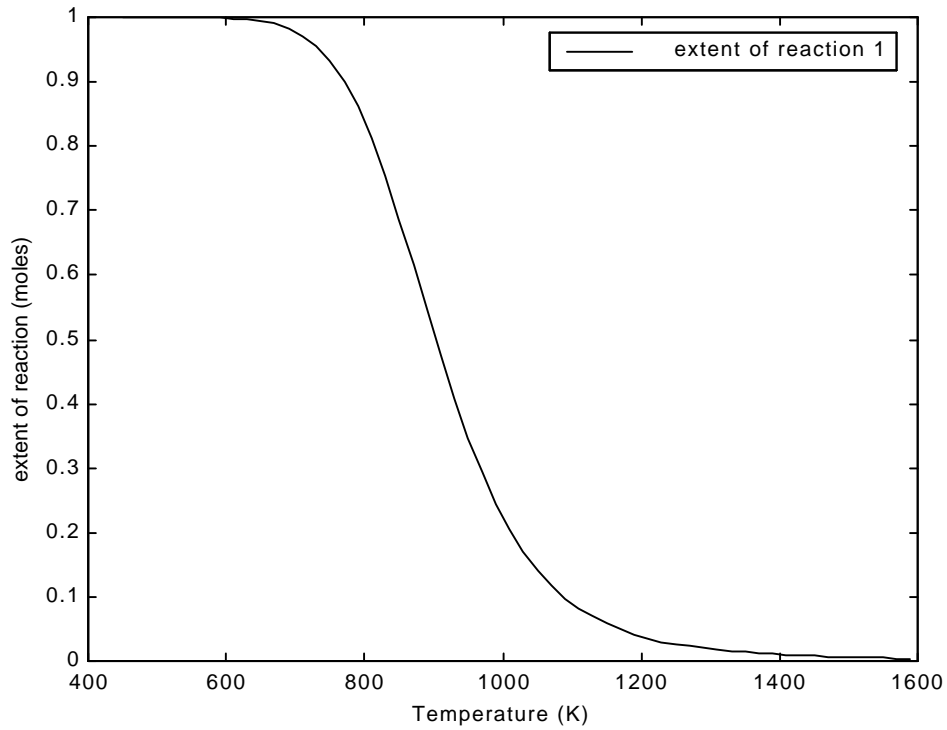


Figure One. Ethyl-Benzene reaction. Extent of reaction as a function of temperature.

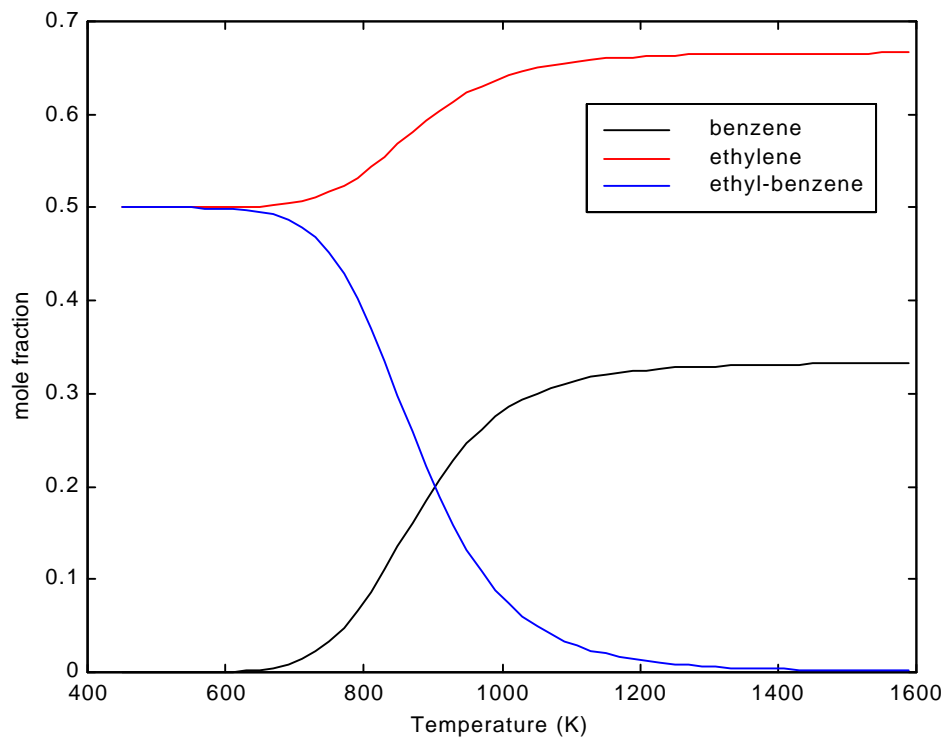


Figure Two. Ethyl-Benzene reaction. Composition as a function of temperature.

B. Adiabatic Case

In the adiabatic problem, the outlet temperature and the extent of reaction are unknown. However, for whatever temperature satisfies the energy balance, the extent of reaction is given by Figure One. Therefore, we can give a consistent initial guess by choosing a temperature and determining the extent of reaction from the isothermal case.

In running the code, I changed the variable, `adiabatic`, to a value of 1 in the code `syseqninput.m`. Also in `syseqninput.m`, I uncommented the line specifying T_{iSO} , which is used as the initial temperature.

If I want to find the equilibrium temperature and compositions for an adiabatic system with initial temperature in the batch reactor of $T_O = 900$ K, we can guess that the adiabatic temperature is 1000K. From Figure 1, we see that this corresponds to an extent of reaction of roughly 0.1.

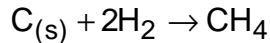
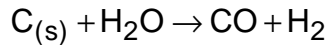
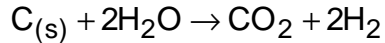
```
» syseqn_all(1,[0.1,1000]);
Attempting solution with MATLABs fsolve function
VARIABLE      INPUT      OUTPUT
    1      1.0000000e-001  2.8787619e-001
    2      1.0000000e+003  9.7169524e+002
```

This guess converges and yields the final extent of reaction of 0.288 and the equilibrium temperature of 971.7 K. The compositions can be obtained from the extent of reaction using equation (35). They will correspond to the compositions at 971.7 K on Figure Two.

In general, it is easier to solve the isothermal problem first. Then, we can use those converged solutions as initial guesses to solve the adiabatic problem. If we don't solve the isothermal problem first, then it becomes more difficult to obtain good initial guesses for the adiabatic problem.

V. EXAMPLE WITH MULTIPLE REACTIONS

Consider the reaction of steam and solid carbon (coal).



We have a batch reactor initially at a pressure of 1 atm and a Temperature, T_0 with 1.0 moles of water and an excess of solid carbon. Because carbon is a solid in excess, we do not need to consider it in the analysis which follows.

The matrix of stoichiometric coefficients is given by:

```
%      CH4      CO      CO2      H2O      H2
nu=[ 0      0  1      -2      2
      0      1  0      -1      1
      1      0  0      0      -2 ];
```

The heats of formation at $T_{\text{ref}} = 298.1 \text{ K}$ are in units of Kcal/mole

```
%      CH4      CO      CO2      H2O      H2      C(s)
DHfref = [-17.889; -26.416; -94.052; -57.7979; 0.0];
```

The heats of formation at $T_{\text{ref}} = 298.1 \text{ K}$ are in units of Kcal/mole

```
%      CH4      CO      CO2      H2O      H2      C(s)
DGfref = [-12.140; -32.808; -94.260; -54.6351; 0.0];
```

For a heat capacity function of the form (cal/mole/K)

$$C_{p,j}(T) = a + 10^{-2}bT + 10^{-5}cT^2 + 10^{-9}dT^3$$

The constants are (columns = chemical species, rows = a,b,c,d)

```
%      CH4      CO      CO2      H2O      H2      C(s)
Cpcon = [ 4.750      6.726      5.316      7.700      6.952
          1.200      0.04001  1.4285      0.04594  -0.04576
          0.3030      0.1283      -0.8362      0.2521      0.09563
          -2.630      -0.5307      1.784      -0.8587      -0.2079];
```

A. Isothermal Case

Find the extent of reaction and composition of the reaction under isothermal conditions, where the initial temperature, T_0 , is the same as the isothermal temperature, T_{ISO} . Do this for the range $400 \text{ K} \leq T_{\text{ISO}} \leq 1600 \text{ K}$.

Using the system of nonlinear algebraic equation solver, `syseqn_all.m`, as we did in the previous example, we simply change the values in `syseqninput.m` to reflect the fact that we have 3 reactions, 5 species, and new

values of the parameters specified above. A copy of the first portion of the input file (where all the changes occur, is given in Appendix C.)

To solve only at 1 temperature, say $T_{\text{iso}}=900$ K, we simply use `syseqn_all.m`. For help on how to use `syseqn_all.m`, type `help syseqn_all` at the Matlab command line prompt. We have three unknowns, the three extents of reaction. We must guess these. I guess [0.25, 0.25, 0.25]. Why? Because I first tried a bunch of other values that didn't work. At the command line prompt, we type:

```
» syseqn_all(1,[0.25,0.15,0.25]);

Attempting solution with MATLABs fsolve function
VARIABLE      INPUT      OUTPUT
    1  2.5000000e-001  2.3335443e-001
    2  1.5000000e-001  3.6799636e-001
    3  2.5000000e-001  1.4003904e-001
```

So the problem converged to a solution of $\underline{\chi} = \begin{bmatrix} 0.2333 \\ 0.3680 \\ 0.1400 \end{bmatrix}$

This tells us that carbon dioxide, carbon monoxide, and methane were all formed. More CO was formed than CO_2 . The amount of methane was formed.

To solve this system for a range of temperatures, we write a short code analogous to that in Appendix B.

A plot of the extent of reaction as a function of the isothermal temperature is shown in Figure 3. A plot of the mole fractions as a function of the isothermal temperature is shown in Figure 4. At low temperatures, the reaction generating carbon dioxide over carbon dioxide is favored. At low temperatures, the hydrogen produced in reaction 1 is largely converted to methane. At high temperatures, the reaction producing carbon monoxide is favored. At high temperatures, the hydrogen produced in reaction 2 does not react to form methane.

B. Adiabatic Case

We can also solve the system under adiabatic conditions. Assume the steam comes in at 900 K. Then find the equilibrium temperature and extents of reaction. We guess an equilibrium temperature and estimate the extents of reaction from Figure Three.

```
» syseqn_all(1,[0.23,0.37,0.14,800]);
Attempting solution with MATLABs fsolve function
VARIABLE      INPUT      OUTPUT
    1  2.3000000e-001  2.6697026e-001
    2  3.7000000e-001  2.1278728e-003
    3  1.4000000e-001  2.3549123e-001
    4  8.0000000e+002  6.3354374e+002
```

This says with steam at 900 degrees in an adiabatic reactor, we converge to a temperature of 633 K. This is because the first two reactions are endothermic. These extents of reaction do indeed match those given by the isothermal case at 633 K in Figure Three. The equilibrium composition of the can be determined from the extents of reaction.

Reminder: Trying to find initial guesses which will converge for the adiabatic problem, without solving the isothermal case first, is like trying to find a needle in a haystack.

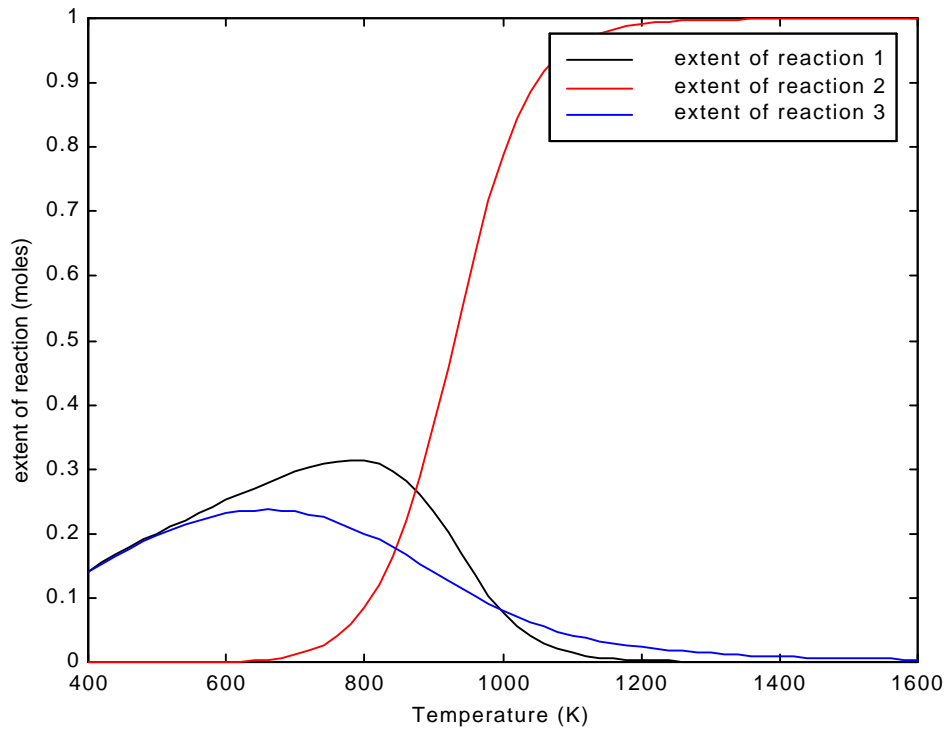


Figure One. Steam-carbon reactions. Extent of reaction as a function of temperature.

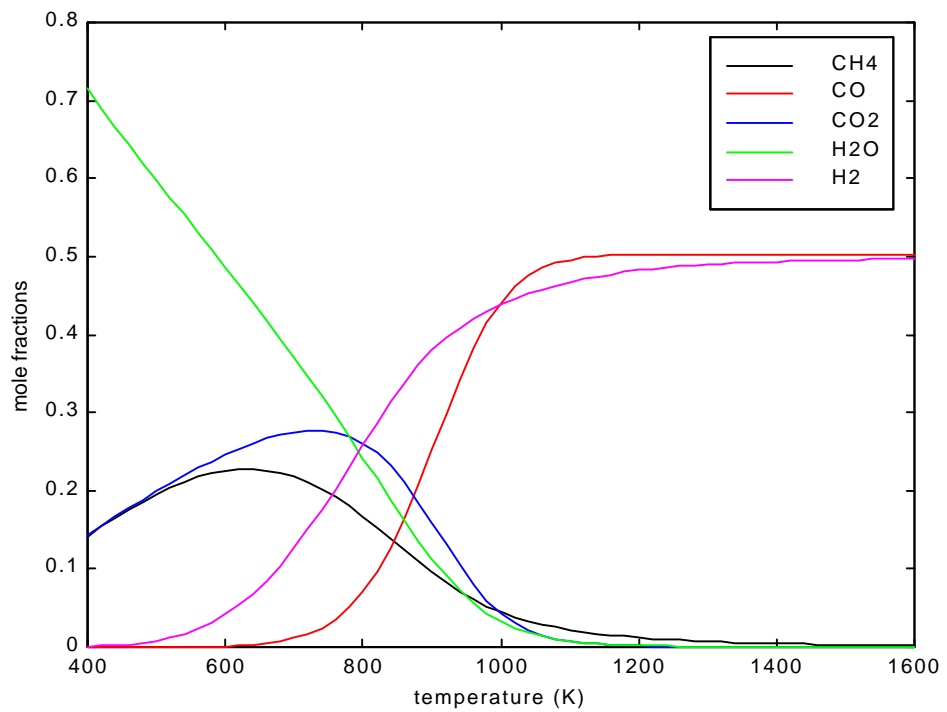
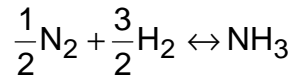


Figure Four. Steam-carbon reactions. Composition as a function of temperature.

VI. TWO MORE EXAMPLES TO WORK YOURSELF

The equilibria of any reactive system can be determined using this technique. Here are two other examples that you might try yourself.

Consider the reaction of benzene and ethylene to form ethyl-benzene



We have a batch reactor initially at a pressure of 1 atm and a Temperature, T_0 with 0.5 moles of nitrogen and 1.5 moles of hydrogen.

The matrix of stoichiometric coefficients is given by: (benzene, ethylene, ethyl-benzene)

```
% N2 H2 NH3
nu=[-1/2 -3/2 1];
```

The heats of formation at $T_{\text{ref}} = 298.1$ K are (benzene, ethylene, ethyl-benzene) in units of Kcal/mole

```
% N2 H2 NH3
DHfref = [0; 0; -10.960];
```

The heats of formation at $T_{\text{ref}} = 298.1$ K are (benzene, ethylene, ethyl-benzene) in units of Kcal/mole

```
% N2 H2 NH3
DGfref = [0.0; 0.0; -3.903];
```

For a heat capacity function of the form (cal/mole/K)

$$C_{p,j}(T) = a + 10^{-2}bT + 10^{-5}cT^2 + 10^{-9}dT^3$$

The constants are (columns = benzene, ethylene, ethyl-benzene, rows = a,b,c,d)

```
% N2 H2 NH3
Cpcon = [6.903 6.952 6.5846
-0.03753 -0.04576 0.61251
0.1930 0.09563 0.23663
-0.6861 -0.2079 -1.5981];
```

Figures Five and Six show plots of what the solution ought to look like:

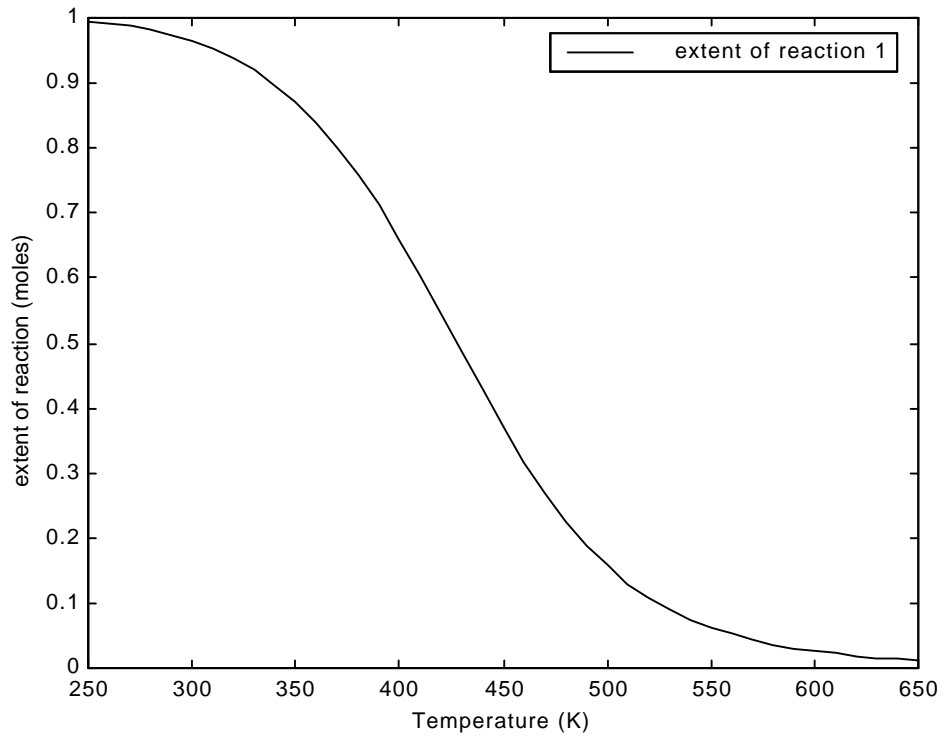


Figure Five. Ammonia reaction. Extent of reaction as a function of temperature.

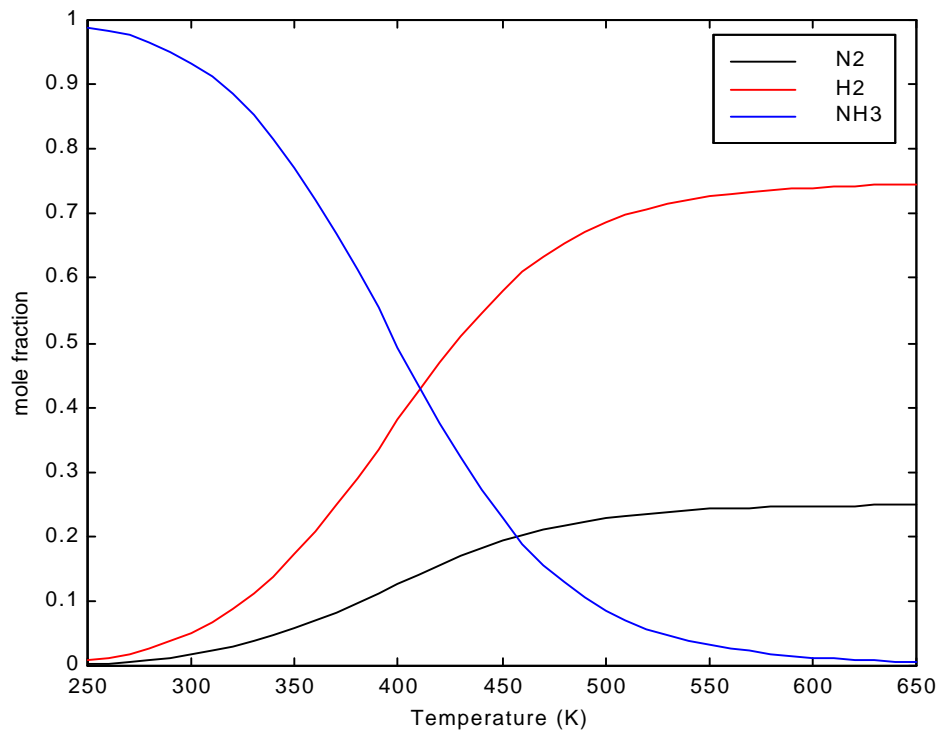
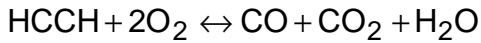
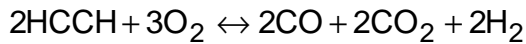
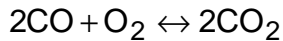


Figure Six. Ammonia reaction. Composition as a function of temperature.

Consider the reactions of an acetylene torch



We have an acetylene torch at a pressure of 1 atm and a Temperature, T_0 with 1.0 moles of acetylene and 2.5 moles of oxygen.

The matrix of stoichiometric coefficients is given by:

```
% HCCH O2 CO CO2 H2O H2
nu=[ 0   -1   -2  2    0    0
     -2   -3    2  2    0    2
     -1   -2    1  1    1    0   ];
```

The heats of formation at $T_{\text{ref}} = 298.1$ K are in units of Kcal/mole

```
% HCCH O2 CO CO2 H2O H2
DHfref = [54.194; 0.0; -26.416; -94.052; -57.7979];
```

The heats of formation at $T_{\text{ref}} = 298.1$ K are in units of Kcal/mole

```
% HCCH O2 CO CO2 H2O H2
DGfref = [50.000; 0.0; -32.808; -94.260; -54.6351; 0.0];
```

For a heat capacity function of the form (cal/mole/K)

$$C_{p,j}(T) = a + 10^{-2}bT + 10^{-5}cT^2 + 10^{-9}dT^3$$

The constants are (columns = chemical species, rows = a,b,c,d)

```
% HCCH O2 CO CO2 H2O H2
Cpcon = [5.21      6.085   6.726   5.316   7.700   6.952
          2.2008  0.3631  0.04001 1.4285  0.04594 -0.04576
          -1.559  -0.1709 0.1283  -0.8362 0.2521  0.09563
          4.349   0.3133 -0.5307  1.784   -0.8587 -0.2079];
```

Figures Seven and Eight show plots of what the solution ought to look like.

You will notice that the plots only cover a small temperature range at very high temperatures. It is only at these conditions that the equations are numerically solvable. At higher temperatures, reaction 3 is negligible and reactions 1 and 2 have the same extent, reducing the system of equations to a single unknown, the extent of reaction 1 or 2. We could continue the plot, solving for only this single unknown.

The numerical convergence problem at the lower temperature is that all of the acetylene is used. This gives an acetylene mole fraction less than 10^{-8} . When this is squared in the denominator to calculate the equilibrium coefficient for reaction 2, we drop below machine precision, and we can't converge. If we want the solution at this point, we need to assume all HCCH is gone and write 2 reactions for the equilibrium between CO with CO_2 and H_2 with H_2O . We could then proceed to lower temperatures.

Extending these plots is left as an exercise to the reader.

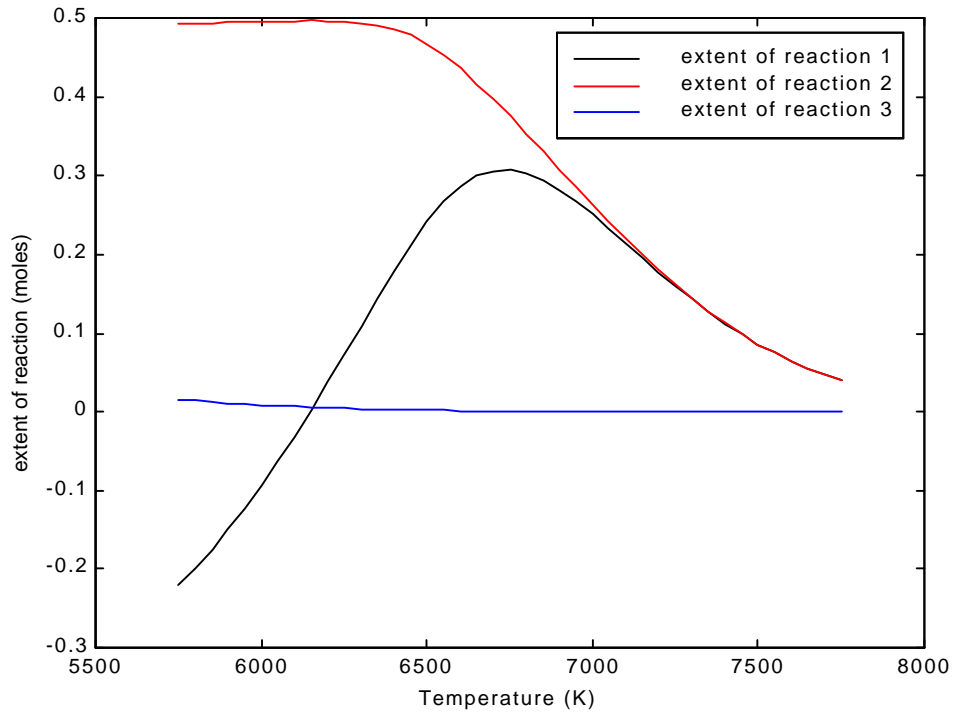


Figure Seven. Acetylene reaction. Extent of reaction as a function of temperature.

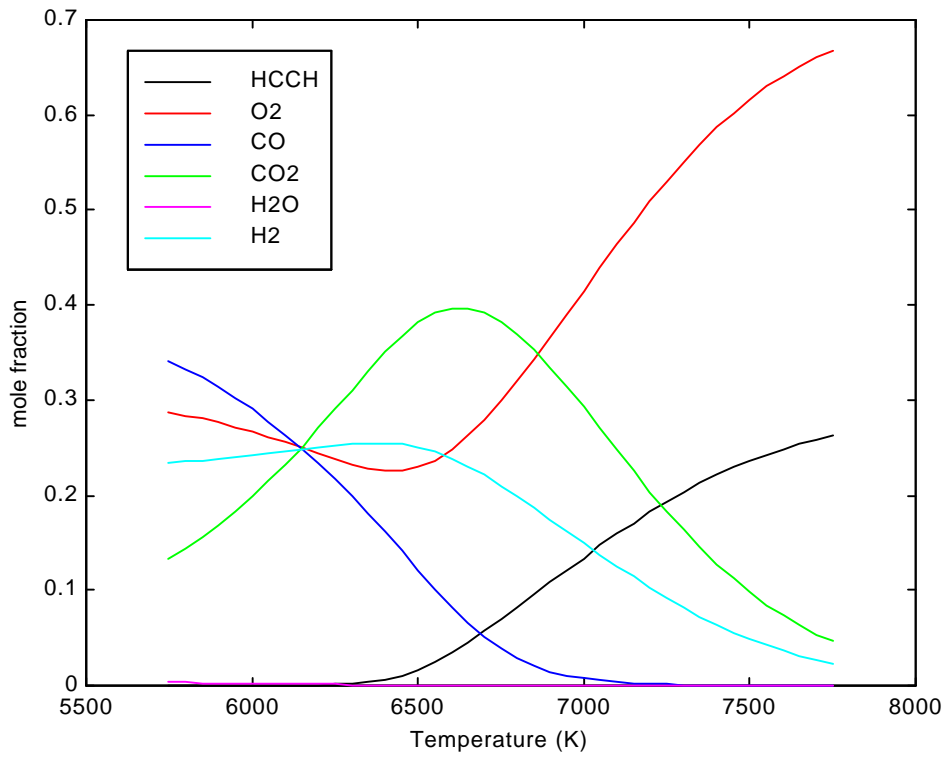


Figure Eight. Acetylene reaction. Composition as a function of temperature.

Appendix A. syseqninput.m MATLAB Code for Example 1.

```

function [f] = syseqninput(x0)
global Tiso xE nc
%
% chemical reaction equilibria calculation
% Benzene plus ethylene to ethyl-benzene
% (Sandler, Second Edition, Illustration 9.7-2 page 561)
%
% Checklist.
% (1) Make sure you have entered the correct number of reactions (nr)
% (2) Make sure you have entered the correct number of components (nc)
% (3) Set adiabatic = 1 for adiabatic system, set adiabatic = 0 for isothermal system
% (4) If the system is isothermal, set the isothermal temperature , (Tiso)
% (5) Enter initial mole amounts of each component (flowin)
% (6) Enter initial temperature of each component (Tin)
% (7) Enter reactor pressure in atmospheres (pressure)
% (8) Enter the stoichiometric matrix
% (9) Enter the heats of formation (Kcal/mol)
% (10) Enter the free energies of formation (Kcal/mol)
% (11) Enter the heat capacity constants
%
% STEP ONE. ENTER PROBLEM SPECIFICATIONS
%
% (1) number of independent chemical reactions
%
nr = 1;
%
% (2)number of components
%
nc = 3;
% in all of the code below
% component 1 is benzene
% component 2 is ethylene
% component 3 is ethyl-benzene
%
% (3) specify whether the system is adiabatic or isothermal
% adiabatic = 0 for isothermal, adiabatic = 1 for adiabatic,
%
adiabatic = 0;
%
% (4) isothermal temperature
% comment this out if you are going to loop through a bunch of temperatures

```

```

%
%Tiso = 600;
%
% (5) inlet flowrates or initial amounts (moles)
%
flowin=zeros(nc,1);
flowin(1) = 1.0;
flowin(2) = 2.0;
%
% (6) inlet temperatures (K)
%
Tin=zeros(nc,1);
Tin(1) = Tiso;
Tin(2) = Tiso;
%
% (7) reactor pressure in atmospheres
%
pressure = 5.0; % put this in atmospheres
pref =1.0; % atmospheres: this is the reference pressure
%
% (8) stoichiometric matrix
% the order is
% benzene ethylene ethyl benzene
%
nu=[-1  -1  1];
%
% reference temperature
%
Tref = 25 + 273.1;
% constants
R = 8.314; % [J/mol/k]
%
% (9) heats of formation at the reference temperature
% from Sandler (Kcal/mol)
% benzene ethylene ethyl benzene
DHfref = [19.820; 12.496; 7.120];
DHfref = DHfref*4.184*1000; % (Joules/mol)
%
% (10) free energies of formation at the reference temperature
% from Sandler (Kcal/mol)
% benzene ethylene ethyl benzene
DGfref = [30.989; 16.282; 31.208];
DGfref = DGfref*4.184*1000; % (Joules/mol)

```

```

%
% (11) heat capacity constants from Sandler Appendix
% Each column contains parameters for a given component.
% The four rows contain the four parameters a, b, c, d for
% Cp = (a + b*T/10^2 + c*T^2/10^5 + d*T^3/10^9) [cal/mole/K]
% benzene ethylene ethyl benzene
%
Cpcon = [-8.650    0.944    -8.398
         11.578    3.735    15.935
         -7.540   -1.993   -10.003
         18.54     4.220    23.95];
for k = 1:nc
    Cpcon(2,k) = Cpcon(2,k)*1.0e-2;
    Cpcon(3,k) = Cpcon(3,k)*1.0e-5;
    Cpcon(4,k) = Cpcon(4,k)*1.0e-9;
end
% convert to correct units (J/mole/K)
Cpcon = 4.184*Cpcon;
%
%   you won't need to touch anything below here.
%
%
% STEP TWO:  LET THE PROGRAM DO ITS WORK
%
%
% STEP TWO A:  Identify unknowns
%
%
% nr extents of reaction
%
X=zeros(nr,1);
for i = 1:nr
    X(i) = (x0(i));
end
%
% 1 Temperature
%
if (adiabatic == 1)
    T = x0(nr+1);
else
    T=Tiso;
end
%

```

```

% STEP TWO B.  DEFINE KNOWNNS
%
%  enthalpy and free energy of formation at arbitrary T
%  (need this for flow out of the reactor term in energy balance)
%
Cpint_T = zeros(1,nc);
Cpint_Tref = zeros(1,nc);
Cpint_Tin = zeros(1,nc);
for k = 1:1:nc
    Temp = T;
    Cpint_T(k) = Cpcon(1,k)*Temp + Cpcon(2,k)/2*Temp^2 + Cpcon(3,k)/3*Temp^3 + Cpcon(4,k)/4*Temp^4;
    Temp = Tref;
    Cpint_Tref(k) = Cpcon(1,k)*Temp + Cpcon(2,k)/2*Temp^2 + Cpcon(3,k)/3*Temp^3 + Cpcon(4,k)/4*Temp^4;
    Temp = Tin(k);
    Cpint_Tin(k) = Cpcon(1,k)*Temp + Cpcon(2,k)/2*Temp^2 + Cpcon(3,k)/3*Temp^3 + Cpcon(4,k)/4*Temp^4;
end
DHf = zeros(1,nc);
DGf = zeros(1,nc);
for k = 1:1:nc
    term2 = Cpcon(1,k)*log(T) + Cpcon(2,k)/2*T + Cpcon(3,k)/6*T^2 + Cpcon(4,k)/12*T^3;
    term3 = Cpcon(1,k)*log(Tref) + Cpcon(2,k)/2*Tref + Cpcon(3,k)/6*Tref^2 + Cpcon(4,k)/12*Tref^3;
    DHf(k) = DHfref(k) + Cpint_T(k) - Cpint_Tref(k);
    DGf(k) = T/Tref*DGfref(k) + (DHfref(k) - Cpint_Tref(k))*(1 - T/Tref) - T*(term2 - term3);
end
%
%  enthalpy and free energy of reaction, equilibrium coefficient at arbitrary T
%
for i = 1:1:nr
    DHr(i) = 0.0;
    DGr(i) = 0.0;
    for k = 1:1:nc
        DHr(i) = DHr(i) + nu(i,k)*DHf(k);
        DGr(i) = DGr(i) + nu(i,k)*DGf(k);
    end
    Ka(i) = exp(-DGr(i)/(R*T));
    %fprintf(1,' %i DHr = %e DGr= %e  K = %e\n',i,DHr(i), DGr(i), Ka(i) );
end
%
%  define molar composition based on extent of reactions
%
xE = flowin;
for i = 1:nr
    for k = 1:nc

```

```

        xE(k) = xE(k) + nu(i,k)*X(i);
    end
end
E = sum(xE);
xE = xE/E;
%
% stream enthalpies
%
heatin = zeros(nc,1);
heatout = zeros(nc,1);
for k = 1:nc
    heatin(k) = flowin(k)*(Cpint_Tin(k) - Cpint_Tref(k));
    heatout(k) = E*xE(k)*(Cpint_T(k) - Cpint_Tref(k));
end
heatintot = sum(heatin);
heatouttot = sum(heatout);
%
% Step Three. Write down nr+1 equations
%
% nr equilibrium constraints
%
for i = 1:nr
    Kcalc(i) = 1;
    for k = 1:nc
        Kcalc(i) = Kcalc(i)*(xE(k)^nu(i,k));
    %     fprintf(1,'rxn = %i comp= %i nu = %i xE = %f fac= %e\n',i,k,nu(i,k),xE(k),(xE(k)^nu(i,k)));
    end
    pfac(i) = (pressure/pref)^(sum(nu(i,:)));
    Kcalc(i) = Kcalc(i)*pfac(i);
    %f(i) = log(Kcalc(i)/Ka(i));
    f(i) = log(Kcalc(i)/Ka(i));
    %fprintf(1,' %i DHr = %e DGr= %e K = %e Kcalc = %e f = %e x = %e\n',i,DHr(i), DGr(i), Ka(i), Kcalc(i),
f(i), x0(i));
end
%
% 1 energy balance, used if system is adiabatic
%
convaidd = 0.001;
heatrxn = 0.0;
for i = 1:nr
    heatrxn = heatrxn + DHr(i)*X(i);
end

```



```
if (adiabatic == 1)
    f(nr+1) = convaid*(heatintot - heatouttot - heatrxn);
end
```

Appendix B. chemeq_loop.m MATLAB Code for Example 1.

```

%
% chemeq_loop
%
global Tiso xE nc
%
% define limits on Temperature range
%
Tlow = 450;
Thigh = 1600;
dT = 20;
T_vec = [Tlow:dT:Thigh];
nT = length(T_vec);
%
% make first initial guess;
%
x0 = [ 9.999998e-001]; % at T = 420
%
nx = length(x0);
%
% loop over temperatures
%
x_store = zeros(nT,nx);
for i = 1:1:nT
    % get current temperature
    Tiso = T_vec(i);
    % call syseqn_all to solve system
    x = syseqn_all(1,x0,0);
    % make new initial guess, old converged value
    x0 = x;
    % store variables for plotting later
    x_store(i,1:nx) = x0(1:nx)';
    % call file once to get compositions at converged value of extent of reaction
    syseqninput(x0);
    xE_store(i,1:nc) = xE(1:nc)';
    % print output to screen
    fprintf(1,'%i %f %e %e %e %e \n', i, Tiso, x, xE);
end

%
% plot results
%

```

```

plot_des{1} = 'k-';
plot_des{2} = 'r-';
plot_des{3} = 'b-';
plot_des{4} = 'g-';
plot_des{5} = 'm-';
plot_des{6} = 'ko';
plot_des{7} = 'ro';
plot_des{8} = 'bo';
plot_des{9} = 'go';
plot_des{10} = 'mo';
%
% Figure one plots extent of reaction vs Temperature
%
figure(1)
for i = 1:1:nx
    plot(T_vec,x_store(:,i),plot_des{i});
    hold on;
end
xlabel('Temperature (K)');
ylabel('extent of reaction (moles)');
legend('extent of reaction 1');
hold off;
%
% Figure one plots mole fractions vs Temperature
%
figure(2)
for i = 1:1:nc
    plot(T_vec,xE_store(:,i),plot_des{i});
    hold on;
end
xlabel('mole fractions');
ylabel('extent of reaction (moles)');
legend('benzene','ethylene','ethyl-benzene');
hold off;

```

Appendix C. portion of syseqninput.m MATLAB Code for Example 2.

```

function [f] = syseqninput(x0)
global Tiso xE nc
%
% chemical reaction equilibria calculation
% Benzene plus ethylene to ethyl-benzene
% (Sandler, Second Edition, Illustration 9.7-2 page 561)
%
% Checklist.
% (1) Make sure you have entered the correct number of reactions (nr)
% (2) Make sure you have entered the correct number of components (nc)
% (3) Set adiabatic = 1 for adiabatic system, set adiabatic = 0 for isothermal system
% (4) If the system is isothermal, set the isothermal temperature , (Tiso)
% (5) Enter initial mole amounts of each component (flowin)
% (6) Enter initial temperature of each component (Tin)
% (7) Enter reactor pressure in atmospheres (pressure)
% (8) Enter the stoichiometric matrix
% (9) Enter the heats of formation (Kcal/mol)
% (10) Enter the free energies of formation (Kcal/mol)
% (11) Enter the heat capacity constants
%
% STEP ONE. ENTER PROBLEM SPECIFICATIONS
%
% (1) number of independent chemical reactions
%
nr = 3;
%
% (2)number of components
%
nc = 5;
% in all of the code below
% component 1 is benzene
% component 2 is ethylene
% component 3 is ethyl-benzene
%
% (3) specify whether the system is adiabatic or isothermal
% adiabatic = 0 for isothermal, adiabatic = 1 for adiabatic,
%
adiabatic = 0;
%
% (4) isothermal temperature
% comment this out if you are going to loop through a bunch of temperatures

```

```

%
%Tiso = 500;
%
% (5) inlet flowrates or initial amounts (moles)
%
flowin=zeros(nc,1);
flowin(4) = 1.0;
%
% (6) inlet temperatures (K)
%
Tin=zeros(nc,1);
Tin(4) = Tiso;
%
% (7) reactor pressure in atmospheres
%
pressure = 1.0; % put this in atmospheres
pref =1.0; % atmospheres: this is the reference pressure
%
% (8) stoichiometric matrix
% the order is
%   CH4      CO      CO2      H2O      H2      C(s)
%
nu=[0      0  1      -2      2
    0      1  0      -1      1
    1      0  0      0      -2 ];
%
% reference temperature
%
Tref = 25 + 273.1;
% constants
R = 8.314; % [J/mol/k]
%
% (9) heats of formation at the reference temperature
% from Sandler (Kcal/mol)
%   CH4      CO      CO2      H2O      H2      C(s)
DHfref = [-17.889; -26.416; -94.052; -57.7979; 0.0];
DHfref = DHfref*4.184*1000; % (Joules/mol)
%
% (10) free energies of formation at the reference temperature
% from Sandler (Kcal/mol)
%   CH4      CO      CO2      H2O      H2      C(s)
DGfref = [-12.140; -32.808; -94.260; -54.6351; 0.0];
DGfref = DGfref*4.184*1000; % (Joules/mol)

```

```

%
% (11) heat capacity constants from Sandler Appendix
% Each column contains parameters for a given component.
% The four rows contain the four parameters a, b, c, d for
%  $C_p = (a + b*T/10^2 + c*T^2/10^5 + d*T^3/10^9)$  [cal/mole/K]
%      CH4      CO      CO2      H2O      H2      C(s)
%
Cpcon = [4.750    6.726    5.316    7.700    6.952
         1.200    0.04001  1.4285   0.04594  -0.04576
         0.3030   0.1283   -0.8362  0.2521   0.09563
        -2.630   -0.5307  1.784    -0.8587  -0.2079];
for k = 1:nc
    Cpcon(2,k) = Cpcon(2,k)*1.0e-2;
    Cpcon(3,k) = Cpcon(3,k)*1.0e-5;
    Cpcon(4,k) = Cpcon(4,k)*1.0e-9;
end
% convert to correct units (J/mole/K)
Cpcon = 4.184*Cpcon;
%
% you won't need to touch anything below here.
%
%
% STEP TWO: LET THE PROGRAM DO ITS WORK
%

```

[Everything below here is unchanged from Appendix A.]