Thermodynamic Studies of High Temperature Equilibria

III. SOLGAS, a Computer Program for Calculating the Composition and Heat Condition of an Equilibrium Mixture

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A computer program named SOLGAS is described. SOLGAS is a program for calculating equilibrium compositions and heat conditions in systems containing ideal gaseous species and pure condensed phases. The method of the equilibrium calculations is based upon minimization of the free energy of the system considered.

In studying high temperature equilibria, *e.g.* equilibria occurring in combustion and metallurgical processes, it is most often necessary to consider several gaseous and condensed species. As soon as several species appear in a system, the calculation of equilibrium compositions becomes quite complicated, and the complexity is strongly dependent on the number of condensed species present. To attack such complex systems, the use of computers is a necessity.

Several calculation *methods* of general interest have been suggested in later years. However, most of them are designed and used for equilibria in a gas phase, while few are devoted to systems containing condensed phases. (Comprehensive reviews are recently published by Zeleznik and Gordon,[1] and by van Zeggeren and Storey,[2] where the main contributions are discussed in detail.)

For calculating the equilibrium conditions in mixtures containing both gaseous and condensed species, the only general *computer program* to be found was HALTAFALL (Ingri *et al.*[3]). This program, primarily intended for water solutions including precipitations, proved to be rather slow applied to high temperature systems containing several condensed phases. For equilibrium studies of some sulfide systems (see, *e.g.*, Eriksson and Rosén [4]), many calculation points were needed. Therefore, it seemed worthwhile to devise a program with considerably higher speed and which also performed heat calculations.

In SOLGAS, the method of free energy minimization, first described by White *et al.*[5] for gas phase equilibria, is extended to systems containing several condensed phases mainly in accordance with Oliver *et al.*[6]

UNITS AND SYMBOLS

1 cal = 1 cal (thermochemical) = 4.184 J.
G = Gibbs free energy in cal.
g = chemical potential in cal mol^{-1}.
H = enthalpy (heat content) in cal mol^{-1}.
K_f = equilibrium constant of formation.
P = total pressure in atm.
p = partial pressure in atm.
R = ideal gas constant (= 1.98717 cal K^{-1} mol^{-1}).
T = absolute temperature in Kelvin.
x^* = number of moles in the initial mixture.
y° = initial guess of the number of moles in the equilibrium mixture.
C_p = heat capacity at constant pressure in cal K^{-1}mol^{-1} as a function of temperature.
$\Delta_f H^\circ_{298}$ = heat of formation at 298.15 K in cal mol^{-1}.
$(G^\circ - H^\circ_{298})/T$ = free energy function in cal K^{-1}mol^{-1}.
$(H^\circ - H^\circ_{298})$ = heat content function in cal mol^{-1}.
Δ = increment of a given property for a reaction (the values for the products less the values for the reactants).
The superscript $^\circ$ indicates the thermodynamic standard state.
The subscript $_{298}$ denotes the reference temperature (25°C = 298.15 K).
The subscript $_f$ denotes the formation of a compound from the elements in their standard states.

METHOD USED FOR THE EQUILIBRIUM CALCULATIONS

For calculating an equilibrium composition, *i.e.* the non-negative set of mole numbers which gives the lowest possible value of the total free energy of the system, and which satisfies the mass balance constraints, an iterative procedure was used. First, the number of moles of the substances considered to be present in the system (y°) are estimated. Improved values of the mole numbers can be calculated (x), which in turn are used for a new guess (y), and so on, until the equilibrium composition is obtained. Thus, every iteration cycle will start with a new set of y-values.

Basic equations. The free energy G of the system can be expressed as

$$G = \sum_i x_i g_i$$

where x_i denotes the mole number of a substance, and g_i is the chemical potential defined as

$$g_i = g_i^\circ + RT \ln a_i$$

For the gaseous species, which are treated as ideal, the activities a_i are equal to the partial pressures p_i:

$$a_i = p_i = (x_i/X)P$$

X and P denote the total number of moles in the gas phase and the total pressure, respectively. For the condensed substances, which are thought to

be pure, the activities are equal to unity. Using the definitions above, a dimensionless quantity (G/RT) can be obtained:

$$G/RT = \sum_{i=1}^{m} x_i^g[(g^\circ/RT)_i^g + \ln P + \ln(x_i^g/X)] + \sum_{i=1}^{s} x_i^c(g^\circ/RT)_i^c \qquad (1)$$

The indices g and c indicate gas phase and condensed phase, respectively. The number of substances in the gas phase is denoted by m, and s is the number of condensed phases assumed to be present at equilibrium.

The value of (g°/RT) for a certain substance is calculated using the expression

$$(g^\circ/RT) = (1/R)[(G^\circ - H^\circ{}_{298})/T] + \Delta_f H^\circ{}_{298}/RT \qquad (2)$$

Alternatively, values of (g°/RT) can be calculated according to the relation

$$\Delta(g^\circ/RT) = -\ln 10 \log K_f$$

The mass balance relations can be written

$$\sum_{i=1}^{m} a_{ij}{}^g x_i^g + \sum_{i=1}^{s} a_{ij}{}^c x_i^c = b_j \quad (j = 1, 2, \ldots, l) \qquad (3)$$

where a_{ij} represents the number of atoms of the jth element in a molecule of the ith substance, b_j is the total number of moles of the jth element, and l is the total number of elements.

The method involves a search for a minimum value of the free energy G of a system (or equivalently (G/RT), see eqn. (1)), subject to the mass balance relations as subsidiary conditions (see eqn. (3)). Lagrange's method of undetermined multipliers is suitable, and the following equations are obtained:

$$(g^\circ/RT)_i^g + \ln P + \ln(x_i^g/X) - \sum_{j=1}^{l} \pi_j a_{ij}{}^g = 0 \quad (i = 1, 2, \ldots, m) \qquad (4)$$

$$(g^\circ/RT)_i^c - \sum_{j=1}^{l} \pi_j a_{ij}{}^c = 0 \quad (i = 1, 2, \ldots, s) \qquad (5)$$

The factors π_j are Lagrangian multipliers.

The eqns. (3) and (4) are expanded in a Taylor series about an arbitrary point $(y_1^g, y_2^g, \ldots, y_m^g; y_1^c, y_2^c, \ldots, y_s^c)$, neglecting terms involving derivatives of second and higher orders:

$$\sum_{i=1}^{m} a_{ij}{}^g y_i^g + \sum_{i=1}^{s} a_{ij}{}^c y_i^c - b_j + \sum_{i=1}^{m} a_{ij}{}^g(x_i^g - y_i^g) + \sum_{i=1}^{s} a_{ij}{}^c(x_i^c - y_i^c) = 0 \quad (j = 1, 2, \ldots, l) \qquad (6)$$

$$(g^\circ/RT)_i^g + \ln P + \ln(y_i^g/Y) - \sum_{j=1}^{l} \pi_j a_{ij}{}^g + (x_i^g/y_i^g) - (X/Y) = 0 \quad (i = 1, 2, \ldots, m) \qquad (7)$$

where $Y = \sum_{i=1}^{m} y_i^g$.

From eqn. (7), x_i^g is calculated:

$$x_i^g = -f_i + y_i^g[(X/Y) + \sum_{j=1}^{l} \pi_j a_{ij}{}^g] \quad (i = 1, 2, \ldots, m) \qquad (8)$$

where

$$f_i = y_i^g[(g^\circ/RT)_i^g + \ln P + \ln(y_i^g/Y)] \quad (i = 1, 2, \ldots, m)$$

The summation of eqn. (8) over i gives

$$\sum_{j=1}^{l} \pi_j \sum_{i=1}^{m} y_i{}^g a_{ij}{}^g = \sum_{i=1}^{m} f_i \tag{9}$$

The quantity C_j, which serves as a correction term in cases where the initial guess of the mole numbers does not satisfy the mass balance relations, is defined according to Levine [7] as

$$C_j = \sum_{i=1}^{m} a_{ij}{}^g y_i{}^g - b_j \quad (j = 1, 2, \ldots, l) \tag{10}$$

Substitution of eqns. (8) and (10) into eqn. (6) gives

$$\sum_{k=1}^{l} \pi_k r_{jk} + [(X/Y) - 1] \sum_{i=1}^{m} a_{ij}{}^g y_i{}^g + \sum_{i=1}^{s} a_{ij}{}^c x_i{}^c = \sum_{i=1}^{m} a_{ij}{}^g f_i - C_j \quad (j = 1, 2, \ldots, l) \tag{11}$$

where

$$r_{jk} = r_{kj} = \sum_{i=1}^{m} (a_{ij}{}^g a_{ik}{}^g) y_i{}^g \quad (j, k = 1, 2, \ldots, l)$$

Now, the eqns. (11), (5), and (9) constitute a system of $(l + s + 1)$ linear equations, consisting of the $(l + s + 1)$ unknown quantities $\pi_j (j = 1, 2, \ldots, l)$, $x_i{}^c$ $(i = 1, 2, \ldots, s)$, and $[(X/Y) - 1]$, the latter, for sake of simplicity, hereafter called π_{l+1}. The system of equations is solved using Gaussian elimination (see, e.g., Ralston [8]). Notice that the solution gives directly the x^c-values, while the x^g-values are obtained from eqn. (8), making use of the values for π_j $(j = 1, 2, \ldots, l + 1)$. It should be mentioned that a singular matrix will be obtained if a mixture of two or more elements reacts completely to one certain substance. The singular matrix can be avoided in two ways: either by choosing the initial mixture so that it deviates minutely from the stoichiometric one, or by adding traces of a new element which reacts with the elements initially added.

Iterative procedure. If all x-values obtained are positive, they will be used as the new initial guess.

If negative x-values appear, the difference between the initial and the calculated values is reduced in order to obtain positive values. For all substances with negative x-values, $y_i{}'$ is put equal to zero where

$$y_i{}' = y_i + \lambda (x_i - y_i) \tag{12}$$

and λ is calculated. Then, eqn. (12) is used to calculate adjusted, positive values of all mole numbers, using a value $\lambda = k\lambda_{min}$, where $k < 1$, and λ_{min} is the smallest λ-value obtained. Usually, k is chosen near unity, *e.g.* 0.99. The y'-values are then used as estimates in the subsequent iteration cycle. Observe, that if the y-values satisfy the mass balance constraints, so do the y'-values, since the mass balance constraints are satisfied for all λ-values.

In order to avoid too many iterations, it was found necessary to adopt a lowest allowed y-value. If the mole number for a substance becomes less than the lowest allowed (in this program 10^{-10} mol), y_i is put equal to zero. That substance will then not be considered in the subsequent iterations, as both x_i and $y_i{}'$ will be zero-valued according to the eqns. (8) and (12), respectively. Moreover, as the x^c-values calculated are independent of the y^c-values, the

program is written so that a condensed compound cannot determine the λ-value, until all x^g-values are positive.

The quantity π_{l+1}, which is a variable in the system of linear equations to be solved, is used to test if the free energy of the system has reached a minimum value. When X approaches Y, $i.e.$ when the improved and the guessed mole numbers are becoming equal, the value of π_{l+1} approaches zero. To achieve a satisfactory accuracy for all mole numbers, it was found that a value of π_{l+1} less than 10^{-8} was adequate. If the test is not satisfied, the calculated y-values are substituted into the eqns. (11), (5), and (9), and a new iteration cycle starts.

Handling of condensed phases. The calculations discussed above are based on certain condensed compounds, initially assumed to be present at equilibrium. However, another set of condensed phases can give a lower value of the free energy of the system, and therefore it must be possible either to withdraw or to add condensed compounds, until the correct set is obtained.

In case the phase rule is contradicted, the condensed compounds taken into account will immediately be cancelled out, and a new set of condensed compounds will be considered. A single condensed compound can also be withdrawn. For example, if the number of moles of a solid becomes more and more negative, that solid will be withdrawn. The same thing will happen if λ for a condensed phase approaches zero.

The free energy of the system can, in addition to eqn. (1), be represented by the equation

$$G/RT = \sum_{j=1}^{l} \pi_j b_j \qquad (13)$$

Eqn. (13) is derived by substitution of the eqns. (4) and (5) into eqn. (1). By considering eqns. (5) and (13), it can easily be checked whether a condensed substance, not primarily assumed, has to be added. That happens if $(g^{\circ}/RT)_i^c$ is less than $\sum_{j=1}^{l} \pi_j a_{ij}^c$. If no additional condensed phases give a lower value of the free energy of the system, the equilibrium phases have been obtained.

As the number of combination alternatives of condensed phases strongly depends on the total number of condensed phases and the number of elements, the greater those numbers, the more iterations will on average be needed to obtain the equilibrium composition, and thus the computing time will be increased. As an example, it can be mentioned that theoretically, 57(794) combination alternatives of condensed compounds exist in a system with 5 elements and a total number of 6(12) condensed phases. To limit the computing time, the calculations will stop after 999 iteration cycles (the figure 999 is arbitrarily chosen and can easily be changed). When a new set of condensed phases is taken into account, a new iteration cycle starts, and all gaseous species will again be considered.

HEAT CALCULATIONS

Since the equilibrium composition has been obtained, the heat generation or the total heat of a process can be computed, using values of $\Delta_f H^{\circ}_{298}$, C_p, and $(H^{\circ} - H^{\circ}_{298})$.

The following scheme is used. The energy necessary for pre-heating the initial mixture from the initial temperature T_1 K to the reaction temperature T K (HP), added to the heat of reaction (HR), gives the total heat (HT):

$$HT = HP + HR$$

HP and HR are given by the following expressions:

$$HP = \sum_i x_i^* (H^\circ - H^\circ_{T_1})_i$$

where x^* denotes the number of moles in the initial mixture, and

$$(H^\circ - H^\circ_{T_1})_i = \int_{T_1}^{T} (C_p)_i \mathrm{d}T$$

$$HR = \sum_i (\varDelta_f H^\circ_T)_i (x_i - x_i^*)$$

where

$$(\varDelta_f H^\circ_T)_i = (\varDelta_f H^\circ_{298})_i + [(H^\circ - H^\circ_{298})_i - (H^\circ - H^\circ_{298})_{\text{elements}}]$$

Observe, that the expression for $(H^\circ - H^\circ_{T_1})$ is not valid for solids with transition points within the actual temperature interval. In that case, $(H^\circ - H^\circ_{T_1})$ has to be computed in advance, using the proper expression.

For substances with $(H^\circ - H^\circ_{298})$ unknown, $\varDelta_f H^\circ$ is supposed to be independent of temperature and equal to $\varDelta_f H^\circ_{298}$.

COMMENTS TO THE PROGRAM SOLGAS

SOLGAS, which is written in the FORTRAN language, can be requested from the author, together with a punching guide. Table 1 shows an example of output of data; the printed values are easily recognized by the text in the headline. It should be mentioned that a value of $x < 10^{-8}$ will be printed as 0.

SOLGAS is dimensioned for 10 elements and 99 substances, of which a maximum of 25 can be condensed. If necessary, these figures can be increased, but they may be sufficient for most systems of practical importance. It should be noted, however, that the computing time is influenced by the number of elements and condensed phases, as discussed above. For a very complex system, a good initial guess can considerably reduce the computing time.

To check the program, calculations were performed on the system (C, H, O, S, Na, N) investigated by Rosén.[9] The results obtained, using SOLGAS, agreed completely with those earlier presented. It could be mentioned that for the calculations performed in Part I,[4] on a system containing maximum 6 solids and 15 gaseous species, the computing time for a calculation point (equilibrium calculations, heat calculations, and calculation of some special quantities for a given set of initial data) was on average about 6 seconds on a computer CD 3200.

It is not quite fair to compare computing times obtained from two different programs, as there are many influencing factors, *e.g.* the language used, output layout, and the initial guesses. However, we have found that the computing time using SOLGAS is of the order $10-100$ times shorter than the calculation

Table 1. An example of output of an equilibrium composition (see Ref. 4).

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T =  1100 K
P = 1.00E 00 ATM


   12 ITERATIONS
              X* MOLE        YO MOLE         X MOLE          P ATM
S2                 0      1.8563E-08     2.3204E-08     4.8621E-10
O2         1.0000E 01     1.5237E-08     1.9046E-08     3.9907E-10
N2         3.7287E 01     2.9829E 01     3.7287E 01     7.8129E-01
AR         4.3779E-01     3.5023E-01     4.3779E-01     9.1732E-03
S                  0      1.0000E-08              0              0
S4                 0      1.0000E-08              0              0
S6                 0      1.0000E-08              0              0
S8                 0      1.0000E-08              0              0
O                  0      1.0000E-08              0              0
SO                 0      2.8313E-05     3.5391E-05     7.4157E-07
SO2                0      7.9998E 00     9.9998E 00     2.0953E-01
SO3                0      9.9647E-05     1.2456E-04     2.6099E-06
S2O                0      2.6284E-08     3.2855E-08     6.8843E-10
NO                 0      1.5704E-07     1.9630E-07     4.1131E-09
NO2                0      1.0000E-08              0              0
CU                 0      1.6000E 01     2.0000E 01              0
CU2O               0              0              0              0
CUO                0              0              0              0
CU2S       1.0000E 01     2.0000E 00     4.4611E-05              0
CUSO4              0              0              0              0
CU2SO5             0              0              0              0


PRE-HEAT =   4.6692E 02 KCAL

HEAT OF REACTION = -5.5703E 02 KCAL

TOTAL HEAT = -9.0106E 01 KCAL
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time using HALTAFALL for one and the same system, containing 2 − 4 solids. If the number of solids is $\gtrsim 5$, HALTAFALL will not reach a solution in a reasonable time.

In many cases it is desirable to obtain values of quantities which are derivable from the mole numbers of the equilibrium mixture. For example, it can be of interest to know the distribution of an element in different species (see, *e.g.*, Eriksson and Rosén [10]), or the values of the partial pressures for some minor substances which appear in negligible amounts, *e.g.* the partial pressure of oxygen in various combustion processes. These calculations can be performed in a subroutine, and the necessary statements are easily written by the user.

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