Solutions of Partial Differential Equations for Mean Molar Functions

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The well known formulas for computing the partial molar functions from a given mean molar function are treated as differential equations for computing the mean molar function from any given partial molar function. Solutions do not depend on the number of components, but only on the choice of three indices: the index d of the dependent mole fraction x_d to be eliminated prior to any computations, the index j of a pivot mole fraction x_j and the index i of the partial molar function y_i. An arbitrary number of additional mole fractions of the other components safe x_d may be linked to the pivot mole fraction x_j. The simple solution: $y = (x_j - \delta_{ij})\, I_{ij}$, $y_i = (x_j - \delta_{ij})^2\, X_{ij}$ and $X_{ij} = d\, I_{ij}/dx_j$ holds for an arbitrary number of components, if the $(c-2)$ mole fractions x_l safe x_d and x_j are transformed to new variables found from the auxiliary equations. Three different cases arise if either $i = d$, $i = j$ or $i \neq d$, $i \neq j$ is chosen. Formulas for the three sets are provided. As an example a simple interpolation formula for ternary systems is discussed.

Previous experimental results on heats of mixing h^M of liquid B-metal binary systems have been evaluated and discussed, using a so called ξ-function [1, 2]

$$h^M = x_2(1 - x_2)\,\xi \qquad (1)$$

as suggested by Wagner [3]. This convenient method however failed in subsequent studies in ternary systems [4]. We had to apply rather intricate computer procedures to find formulas for h^M and the three partial molar heats h_i^M. Therefore we tried to find simpler methods to process data in ternary systems with simple programmable desk calculators.

A thorough study of pertinent formulas and methods seemed to indicate a missing link in the theory of such functions: Experimental values of excess chemical potentials $\mu_i^E = RT \ln \gamma_i$ ($\gamma_i =$ activity coefficient) in binary systems usually are evaluated by integration of the so called Gibbs-Duhem-equation [3]. In ternary systems integration is possible along particular paths of integration, e.g. $x_2/x_3 = $ constant, as shown by Darken [3, 5, 6]. Another solution by Wagner [3] introduces besides x_2 a new variable $y = n_3/(n_1 + n_3)$ in the Gibbs-Duhem-equation. Our previous attempts to find reasonable formulas by trial and error always rendered functions with quotients of mole fractions. Therefore we supposed some hidden reason for the efficiency of such quotients.

Trouble with such functions seems to have a simple reason: Extensive functions $Y = Y(T, p, n_l)$ are homogeneous functions of the first degree of the c independent mole numbers n_l (c number of components). Therefore we get with Euler's equation

$$Y = \sum n_l\, y_l \quad \text{with the definition}$$
$$y_l = (\partial Y/\partial n_l)_{T,p,n_k}, \quad k \neq l \qquad (1)$$

and the more useful differential

$$\mathrm{d}Y = \sum y_l\, \mathrm{d}n_l \qquad (2)$$

with a short proof. (By partial differentiation to some n_k of (1) we get:

$$\sum_l n_l\,(\partial y_l/\partial n_k) = 0\,,$$

therefore too

$$\sum_k \sum_l n_l(\partial y_l/\partial n_k)\cdot \mathrm{d}n_k = 0 \quad \text{and}$$
$$\sum_l n_l\, \mathrm{d}y_l = 0\,.$$

So the differential of (1) renders (2). The differentials $\mathrm{d}y_l$ are more versatile, because they can be expanded with any set of appropriate variables of composition.)

In practice, however, the mean molar functions $y = y(T, p, x_l)$ are studied, because the number of independent variables of composition is reduced to $(c-1)$ because of

$$\sum x_l = 1 \quad \text{and} \quad \sum \mathrm{d}x_l = 0\,. \qquad (3)$$

In this way labour with experiments and computations is reduced by an order of degree. But this results inevitably in more trouble with formulas.

First we have to find how to deal with the new functions and variables. Of course we can derive at once from (1) by division with the sum of number of moles n

$$y = \sum x_l y_l \quad \text{and} \quad dy = \sum y_l \, dx_l \qquad (4)$$

(because from $\sum n_l \, dy_l = 0$, too $\sum x_l \, dy_l = 0$).

Such "symmetric" formulas, however, still comprise a dependent mole fraction x_d, that may be choosen arbitrarily from the c mole fractions in c different ways, and has to be eliminated prior to any computations by

$$x_d = 1 - \sum{}^{(d)} x_l \quad \text{and} \quad dx_d = -\sum{}^{(d)} dx_l \qquad (5)$$

by separation of x_d in (3) (the symbol $\sum^{(d)}$ indicates, that the term with the index d has been omitted from the sum). From (4) we get

$$y = x_d y_d + \sum{}^{(d)} x_l y_l \quad \text{and}$$
$$dy = y \, dx_d + \sum{}^{(d)} y_l \, dx_l \qquad (4\,\text{a})$$

and using (5) finally

$$y = y_d + \sum{}^{(d)} x_l (y_l - y_d) \quad \text{and}$$
$$dy = \sum{}^{(d)} (y_l - y_d) \, dx_l . \qquad (6)$$

Clearly the structure of such "asymmetrical" formulas will be determined by the choice of the index d of the dependent mole fraction x_d, to be eliminated prior to computations. From (6) we finally get the partial derivatives of the new function y with respect to the new variables x_l:

$$(\partial y / \partial x_l)_{T, p, x_m} = y_l - y_d , \quad m \neq l \qquad (7)$$

only rendering $(c-1)$ equations for the unknown c functions y_l. Therefore we have to use (6) as additional equation, rendering

$$y_d = y - \sum{}^{(d)} x_l (\partial y / \partial x_l) \qquad (8)$$

as shown by Haase [7, 8].

Clearly the relations between y and the y_l are much more intricate than the simple formulas (1) for Y and y_l in terms of the mole numbers n_l.

Sometimes in physics the functions and variables found at first sight are not the most efficients ones with reference to the mathematics involved, as known from theoretical mechanics. Therefore we tried to find other functions and variables, rendering at least one partial molar function as a simple derivative of a function of the molar function.

This problem will be solved by treating the equations for computing the partial molar functions by partial differentiation of the given mean molar function as partial differential equations for the mean molar function, if some partial molar function y_i is given. As new function we get the so called integral control function I_{ij} in terms of a pivot mole fraction x_j and $(c-2)$ new variables q_{lj}, r_{lj}, of f_{lj}, depending on the three different possibilities of choosing $i = d$, $i = j$, or $i \neq d$, $i \neq j$. The new variables, q_{lj} for quotient, r_{lj} for ratio and f_{lj} for fraction, are quotients of mole fractions, as presumed before. The new functions and variables will be treated as shown with y in terms of the x with formulas (4 a), (6), (7) and (8), starting with the differential dI_{ij}. Of course we shall meet the same trouble, because in this case too only $(c-1)$ partial derivatives can be found. This is only a question of the number of independent variables and not of the kind of variables. But we can find one equation rendering a function of a partial molar function as a simple partial derivative of I_{ij} with respect to the pivot mole fraction x_j.

Later applications are possible without going through the subsequent expositions. Some simple applications and an interpolation formula for ternary system are provided on the last pages. The practical application has to be left to subsequent papers in view of the amount of computations involved. It will take some more papers to deal with the more intricate case of systems with electron transfer [4].

1. Control Functions

From (7) and (8) we get a formula for any partial molar function [4]

$$y_i = y - \sum{}^{(d)} (x_l - \delta_{il}) (\partial y / \partial x_l) \qquad (9)$$

using the Kronecker-symbol $\delta_{il} = 0$ for $i \neq l$ and $\delta_{il} = 1$ for $i = l$. For any pure component i, given by $x_i = 1$, all other $x_l = 0$, always $y_i = y$ holds. Therefore, any factor in the sum of (9) has to become zero for $x_i = 1$, all $x_l = 0$. By this reason we get factors x_l, but $(x_i - 1)$ in (9). In the binary case we get with $x_j = x_1$ or $x_j = x_2$ the general formula

$$y_i = y - (x_j - \delta_{ij}) (\partial y / \partial x_j). \qquad (10)$$

We first tried to get as simple functions and symbols as possible for binary systems. Obviously the structure of the formulas only depend from the indices i and j. Therefore the following functions

and symbols were choosen [9, 10]

$$y = -(x_j - \delta_{ij}) I_{ij} \quad \text{and}$$
$$y_i = (x_j - \delta_{ij})^2 X_{ij}. \tag{11}$$

Putting (11) to (10) the simple partial differential

$$X_{ij} = (\partial I_{ij}/\partial x_j) \tag{12}$$

results. X_{ij} and I_{ij} were called control function and integral control function (german: Formfunktion), because such functions carry the information on a particular function in some system, and control the shape of the graphs.

Darken [6] recast (10) to

$$\frac{y_i}{(x_j - \delta_{ij})^2} = \frac{d}{dx_j}\left(\frac{-y}{(x_j - \delta_{ij})}\right) \tag{13}$$

and called the left side function X_{ij} "alpha" and "beta" function, but seemingly did not pay particular attention to the function on the right side. The integral control function I_{ij} is related to the apparent molar functions [9]. Clearly Darken's formula (13) is identical with our formulation (12), but obviously could not be applied to the multicomponent case given by (9).

2. The Binary Case

Arranging (10) to

$$(x_j - \delta_{ij}) y' - y = -y_i \tag{14}$$

we get a simple differential equation to compute y from any given y_i with the solutions

$$y = -(x_j - \delta_{ij}) C$$
$$dC/dx_j = y_i/(x_j - \delta_{ij})^2. \tag{15}$$

Clearly $C = I_{ij}$, and the functions I_{ij} and X_{ij} are solutions of (14).

To get uniform symbols (1) has been replaced by

$$y^M = -x_j(x_j - 1) X_j \tag{16}$$

but the control function X_j is not a solution of (14) and therefore only useful in binary systems.

3. The Multicomponent Case

Arranging (9) we get a partial differential equation

$$\sum (x_l - \delta_{il})(\partial y/\partial x_l) = y - y_i \tag{17}$$

for computing y from a given partial molar funtion y_i. Lagrange's auxiliary equations, for convenience written in reverse order

$$\frac{dy}{y - y_i} = \frac{dx_1}{x_1 - \delta_{i1}} = \frac{dx_2}{x_2 - \delta_{i2}} = \cdots$$
$$= \frac{dx_j}{x_j - \delta_{ij}} = \cdots = \frac{dx_c}{x_c - \delta_{ic}} \tag{18}$$

suggest the arbitrary choice of a pivot mole fraction x_j. (Of course, in (17) and (18) the dependent mole fraction x_d is absent. If $d = 1$, $d = 2$ or $d = c$, such terms have to be omitted.)

Connecting first dy and dx_j we arrive at

$$(x_j - \delta_{ij}) dy = (y - y_i) dx_j \tag{14a}$$

identical with (14). The solutions (11) and (12) of the binary case hold even with an arbitrary number of components, if the following solutions for the other $(c - 2)$ independent mole fractions x_l are taken in account. For all other mole fractions x_l except x_d and $\boldsymbol{x_j}$ we find simple proportionality from

$$(x_l - \delta_{il}) = k(x_j - \delta_{ij}). \tag{19}$$

After fixing the indices d and j of x_d and x_j obviously three different sets of solutions arise by choice of the index i of the partial molar function y_i.

3.1. The q_{lj}-set with $i = d$

Taking y_i as y_d, the Kronecker-symbols in (18) and (19) will vanish rendering from (19)

$$x_l = q_{lj} x_j. \tag{20}$$

The limiting values of the so defined new variables q_{lj} are $q_{lj} = 0$ for $x_l = 0$, but for $x_j = 0$ the q_{lj} become infinite in any subsystem not containing the component j. This may limit the practical use of this set.

3.2. The r_{lj}-set with $i = j$

Taking y_i as y_j the Kronecker-symbols δ_{jl} will vanish, but of course $\delta_{jj} = 1$. From (19) follows

$$x_l = r_{lj}(1 - x_j) \tag{21}$$

defining new variables r_{lj} with the convenient limiting values $r_{lj} = 0$ for $x_l = 0$, and $r_{lj} = 1$ for $x_l = 1$.

3.3. The f_{lj}-set with $i \neq d$, $i \neq j$

When choosing the index i different from d or j, e.g. $i = f$, the corresponding mole fraction x_f will appear in (18) or (19) in a bracket $(x_f - 1)$, whereas

all other Kronecker-symbols will vanish. From (19) follows a new set of variables

$$(1 - x_f) = f_{fj} x_j \quad \text{and} \quad x_l = f_{lj} x_j . \tag{22}$$

The f_{lj} will show the same limiting values as the q_{lj}, putting the same limitations on this set.

$$\mathrm{d}I_{ij} = \frac{[y_d + \delta_{ij}(y_j - y_a)] \, \mathrm{d}x_j + \sum^{(d,j)} (y_l - y_a) \, [x_l \, \mathrm{d}x_j - (x_j - \delta_{ij}) \, \mathrm{d}x_l]}{(x_j - \delta_{ij})^2} , \quad l \neq d, \quad l \neq j . \tag{24}$$

In the binary case, any $x_l = 0$ and $\mathrm{d}x_l = 0$, we get again the solution (11) and (12). With three and more components obviously (24) has to be reduced by judicious choice of new variables to arrive at fairly simple expressions. Any set of new variables can be tested by inserting in (24).

5. Formulas for the R-set

According to 3.2 we put $i = j$ and $\delta_{jj} = 1$. Inserting (21) and

$$\mathrm{d}x_l = (1 - x_j) \, \mathrm{d}r_{lj} - r_{lj} \, \mathrm{d}x_j \tag{25}$$

wet get from (24)

$$\mathrm{d}I_{jj} = \frac{y_j \, \mathrm{d}x_j + (x_j - 1)^2 \sum^{(d,j)} (y_l - y_a) \, \mathrm{d}r_{lj}}{(x_j - 1)^2} . \tag{26}$$

Defining the symbols

$$X_{jj} = \left(\frac{\partial I_{jj}}{\partial x_j} \right)_{r_{lj}} , \quad R_{lj} = \left(\frac{\partial I_{jj}}{\partial r_{lj}} \right)_{x_j, r_{kj}} , \, k \neq l , \tag{27}$$

we get the formulas

$$y_j = (x_j - 1)^2 X_{jj} \quad \text{and} \quad y_l - y_a = R_{lj} . \tag{28}$$

Unfortunately we get only one simple formula for y_j, when using the convenient variables r_{lj}. For all other partial molar functions we have first to assess y_a by inserting (21) and (28) in (6), arranging to

$$y = y_a(1 - x_j) + x_j y_j + \sum^{(d,j)} r_{lj} R_{lj} (1 - x_j) \tag{29}$$

dividing by $(1 - x_j)$, noting (3) and (28) and finally arriving at

$$y_a = I_{jj} - x_j(1 - x_j) X_{jj} - \sum^{(d,j)} r_{lj} R_{lj} . \tag{30}$$

Any other partial molar function besides y_j and y_a is found by

$$y_k = y_a + R_{kj} \tag{31}$$

4. The Differential $\mathrm{d}I_{ij}$

Subsequent computations can be reduced by first assessing the differential of I_{ij} (11)

$$\mathrm{d}I_{ij} = \frac{y \, \mathrm{d}x_j - (x_j - \delta_{ij}) \, \mathrm{d}y}{(x_j - \delta_{ij})^2} . \tag{23}$$

Inserting (6) and arranging we get

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or fully

$$y_k = I_{jj} - x_j(1 - x_j) X_{jj} - \sum^{(d,j)} (r_{lj} - \delta_{lk}) R_j . \tag{32}$$

6. Formulas for the Q- and F-set

Proceeding in the same way we get the following definitions and formulas for use with the less convenient variables q_{lj} and f_{lj} according (20) and (22)

$$X_{dj} = \left(\frac{\partial I_{dj}}{\partial x_j} \right)_{q_{lj}} , \quad Q_{lj} = \left(\frac{\partial I_{dj}}{\partial q_{lj}} \right)_{x_j, q_{kj}} k \neq l , \tag{33}$$

$$y_d = x_j^2 X_{dj} , \quad y_l = y_d - Q_{lj} \tag{34}$$

or fully

$$y_l = x_j^2 X_{dj} - Q_{lj} , \tag{34a}$$

$$y_j = - I_{dj} - x_j(1 - x_j) X_{dj} + \sum^{(d,j)} q_{lj} Q_{lj} \tag{35}$$

and for the F-set

$$X_{fj} = \left(\frac{\partial I_{fj}}{\partial x_j} \right)_{f_{lj}} , \quad F_{fj} = \left(\frac{\partial I_{fj}}{\partial f_{fj}} \right)_{x_j, f_{lj}} ,$$

$$F_{lj} = \left(\frac{\partial I_{fj}}{\partial f_{lj}} \right)_{x_j, f_{kj}} , \quad k \neq j , \tag{36}$$

$$y_f = x_j^2 X_{fj} , \quad y_d = x_j^2 X_{fj} - F_{fj} ,$$
$$y_l = x_j^2 X_{fj} - F_{fj} - F_{lj} , \tag{37}$$

$$y_j = - I_{fj} + x_j(x_j - 1) X_{fj} + (f_{fj} - 1) F_{fj} + \sum^{(d,f,j)} f_{lj} F_{lj} . \tag{38}$$

The functions I_{ij} follow from the definition (11):

$$y = - (x_j - 1) I_{jj} , \quad y = - x_j I_{dj} ,$$
$$y = - x_j I_{fj} \tag{39}$$

substituting the new variables from the R-, Q- or F-set for the $(c - 2)$ mole fractions x_l besides the eliminated x_d and the pivot mole fraction x_j.

Formulas for the Q- and F-set are simpler, than for the R-set. Therefore the Q-set may be useful, if the limiting behaviour of the variables q_{lj} for $x_j = 0$ is of no importance. The somewhat more complicated F-set seems to offer no advantages at present.

7. Examples

Prior to computations in multicomponent systems some attention should be paid to the judicious choice of the indices d, i, j and l. Experimental data of some ternary excess chemical potential μ_i^E may be processed by choosing $i = 1, 2$ or 3. But then in view of the advantages of the variables r_{lj} we should prefer $j = i$ to apply the R-set. After fixing i and $j = i$, we are free to eliminate one of both remaining mole fractions as the dependent variable x_d. Then the remaining mole fraction is the x_l, to be eliminated by r_{lj}. Putting e.g. $i = 3$, we take x_3 as pivot mole fraction x_j. Then we may eliminate $x_1 = x_d$, and take x_2 as remaining x_l, to be replaced by $r_{23} = x_2/(1 - x_3)$. In this way we get the indices $i = j = 3$, $d = 1$ and $l = 2$. (In systems with c components we get $(c - 2)$ different mole fractions x_l and therefore as much different indices l.) The numbers of indices have to be put into the general equations of the R-set, e.g. $X_{33} = \mu_3^E/(1 - x_3)^2$ and $dI_{33}/dx_3 = X_{33}$. Keeping x_2/x_3 constant in Darken's method in ternary systems clearly points to variables of the Q-set. In view of (20) we have $x_l = x_2$ and $x_j = x_3$. As $x_2 = q_{23} x_3$, this method means to replace x_2 by q_{23}, and to keep q_{23} constant. This means too, to eliminate x_1 as the x_d. Wagner's variable

$$y = n_3/(n_1 + n_3) = x_3/(1 - x_2)$$

is related to the R-set by choosing $j = 2$, $l = 3$ and therefore $d = 1$. In view of (21) we get $x_3 = r_{32}(1 - x_2)$ and $y = r_{32}$ in our system.

In ternary systems mean molar functions y can be represented by a power series expansion

$$y = \sum_k \sum_l a_{kl} x_2^k x_3^l . \tag{40}$$

Obviously $x_1 = x_d$ or $d = 1$. Using (9) the following formulas for the three partial molar functions are found

$$y_1 = \sum_k \sum_l (1 - k - l) a_{kl} x_2^k x_3^l , \tag{41}$$

$$y_2 = \sum_k \sum_l [(1 - k - l) x_2 x_3 + k x_3] \\ \cdot a_{kl} x_2^{k-1} x_3^{l-1} , \tag{42}$$

$$y_3 = \sum_k \sum_l [(1 - k - l) x_2 x_3 + l x_2] \\ \cdot a_{kl} x_2^{k-1} x_3^{l-1} . \tag{43}$$

In this case, the coefficients of y_1 are simple multiples of the coefficients a_{kl} of y.

Choosing x_3 as pivot mole fraction x_j, $j = 3$, and preferring the Q-set for ease of computation we get

$$x_2 = q_{23} x_3 . \tag{44}$$

Putting (44) to (40) and dividing by $(-x_3)$ we get regarding (11) and (39)

$$I_{13} = - \sum_k \sum_l a_{kl} q_{23}^k x_3^{k+l-1} \tag{45}$$

and by differentiation with respect to x_3 and q_{23} in view of (33)

$$X_{13} = \sum_k \sum_l (1 - k - l) a_{kl} q_{23}^k x_3^{k+l-2} , \tag{46}$$

$$Q_{23} = - \sum_k \sum_l k a_{kl} q_{23}^{k-1} x_3^{k+l-1} . \tag{47}$$

Putting I_{13}, X_{13} and Q_{23} in (34) and (35) and finally again substituting x_2 for $q_{23} x_3$ the formulas (41), (42) and (43) are obtained.

8. A Simple Interpolation Formula for Ternary Systems

The rather lengthy and tedious computations for assessing the matrix A_{kl} in (40) from experimental data may be considerably reduced by first computing approximate data from the formulas for the binary subsystems using a simple interpolation formula. According to our experience with ternary metallic systems even simple interpolation formulas render about 90% of the experimental values. As the precision of such data only seldom approaches 1%, the precision of the residue will at best approach 10%. Therefore a simple additional procedure for assessing a matrix for the residue will suffice as a rule.

To assemble interpolation formulas for systems with c components from the formulas for the binary subsystems we have to use some additional indices to indicate different systems. Tentatively, — we have still to gather more experience —, the following method is adopted: the numbers of the components are indicated in an additional index. The first number is the index of the mole fraction not used in the formula. In subsystems without the

component d this will be another mole fraction than x_d.

In a ternary system y^{123} means the formula for the mean molar function y in terms of x_2 and x_3. y^{23} is the formula for the binary system with the components 2 and 3 in terms of x_3.

Choosing x_1 as the dependent mole fraction x_d and x_3 as the pivot mole fraction x_j, and finally putting $x_2 = r_{23}(1 - x_3)$ according to (21) the following simple formula

$$y^{123} = y^{13} + r_{23}(y^{23} - y^{13}) + (1 - x_3)^2 y^{12} \quad (48)$$

allows for linear interpolation between the binary systems (13) and (23), whereas the third system (12) is interpolated by multiplying with $(1 - x_3)^2$, as done previously by Kohler [10].

In y^{12} the variable x_2 has to be substituted by r_{23} to stay within the limiting values 0 and 1 of x_2.

To get the formulas for the three partial molar functions the following procedure is applied:

1. According to (39) we get by division with $(1 - x_3)$

$$I_{33}^{123} = I_{33}^{13} + r_{23}(I_{33}^{23} - I_{33}^{13}) + (1 - x_3) y^{12}. \quad (49)$$

2. Differentiation with respect to x_3 and r_{23} renders

$$X_{33}^{123} = X_{33}^{13} + r_{23}(X_{33}^{23} - X_{33}^{13}) - y^{12}, \quad (50)$$

$$R_{23}^{123} = I_{33}^{23} - I_{33}^{13} + (1 - x_3)(y^{12})' \quad (51)$$

with $(y^{12})' = dy^{12}/dr_{23}$.

3. y_1 as y_d follows from (30) using (49), (50) and (51) as

$$y_1 = I_{33}^{13} - x_3(1 - x_3)[X_{33}^{13} + r_{23}(X_{33}^{23} - X_{33}^{13})] + (1 - x_3^2) y^{12} - r_{23}(1 - x_3)(y^{12})'. \quad (52)$$

4. According to (28) y_2 is found by simply adding (51) to y_1

$$y_2 = I_{33}^{23} - x_3(1 - x_3)[X_{33}^{13} + r_{23}(X_{33}^{23} - X_{33}^{13})] + (1 - x_3^2) y^{12} - (r_{23} - 1)(1 - x_3)(y^{12})'. \quad (53)$$

5. y_3 is found by multiplying (50) with $(1 - x_3)^2$ according to (28).

Two different checks for such formulas may be applied:

1. Putting the variables equal 0 or 1 and checking the borderline behaviour. Putting e.g. $x_3 = 0$ (52) reduces to $(I_{33}^{13} = 0$ for $x_3 = 0)$

$$y_1 = y^{12} - r_{23}(dy^{12}/dr_{23}) \quad (52\,\text{a})$$

being the formula for y_1^{12} in terms of r_{23}.

2. Putting the three partial molar functions in (6) formula (48) will be found.

Applications to evaluations of heats of mixing and of molar free energies of mixing in ternary systems will be presented in subsequent papers. As long as the functions for the binary systems may be represented by power series, the formulas (48)—(53) provide fairly simple rules for assembling matrices for the ternary functions.

[1] F. E. Wittig, Z. Elektrochem. **63**, 327 (1959).
[2] F. E. Wittig and G. Keil, Z. Metallkunde, **54**, 576 (1963).
[3] C. Wagner, Thermodynamics of Alloys, Addison-Wesley Press, Inc., Cambridge 42, Mass. 1952.
[4] F. E. Wittig, N. Saes and W. Waldherr, Rev. Chim. Minér. **9**, 71 (1972).
[5] L. S. Darken, J. Amer. Chem. Soc. **72**, 2909 (1950).
[6] L. S. Darken, R. W. Gurry, and M. B. Bever, Physical Chemistry of Metals, McGraw-Hill Book Company, Inc., New York 1953.
[7] R. Haase, Z. Naturforsch. **3a**, 285 (1948).
[8] R. Haase, Thermodynamik der Mischphasen, Springer-Verlag, Berlin 1956.
[9] F. E. Wittig, Chemie-Ing. Technik **42**, 1037 (1970), 43, 1211 (1971).
[10] F. Kohler, Monatsh. Chem. **91**, 738 (1960).